

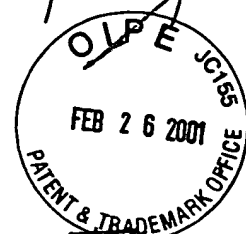
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

First Named
Inventor : Reitz et al.
Appln. No.: 09/433,202
Filed : November 4, 1999
For : PARTICLE DISPERSIONS
Docket No.: N19.12-0026

Appeal No. ---

Group Art Unit: 1755

Examiner: M.
Marcheschi



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TRANSMITTAL OF APPEAL BRIEF
(PATENT APPLICATION - 37 C.F.R. § 192)

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Commissioner for Patents
Washington, D.C. 20231

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8 / DAY OF February 2001.
Peter S. Dardi
PATENT ATTORNEY

Sir:

Transmitted herewith in triplicate is the Appeal Brief in
this application with respect to the Notice of Appeal filed on
December 21, 2000.

FEE STATUS

[X] Small entity status under 37 C.F.R. §§ 1.9 and 1.27
is established by a verified statement.

FEE FOR FILING APPEAL BRIEF

Pursuant to 37 C.F.R. 1.17(c) the fee for filing the
Appeal Brief is \$155.00.

The Commissioner is authorized to charge any additional
fees associated with this paper or credit any overpayment to Deposit
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Respectfully submitted,

WESTMAN, CHAMPLIN & KELLY, P.A.

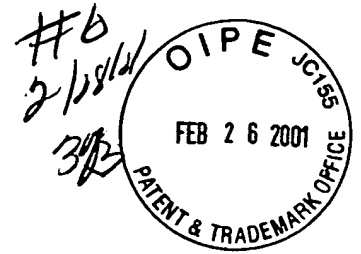
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Marcheschi

BRIEF FOR APPELLANT

BOX AF
Assistant Commissioner of Patents
Washington, D.C. 20231

I HEREBY CERTIFY THAT THIS PAPER IS
BEING SENT BY U.S. MAIL, FIRST
CLASS, TO THE DIRECTOR OF PATENTS,
WASHINGTON, D.C. 20231, THIS

21 DAY OF February, 2001.
R. L. D. Ranch
PATENT ATTORNEY

Sir:

This is an appeal from an Office Action dated September 25, 2000 in which claims 1 - 28 and 31 were finally rejected. The pending claims are reproduced in Appendix A, below. In the Final Office Action of September 25, 2000, the Examiner objected to the application papers. Applicants believe that this objection has been overcome.

Applicants file herewith a Terminal Disclaimer over copending Applications 09/085,514 and 09/136,483. These Terminal Disclaimers obviate Obviousness-type Double Patenting Rejections Over these applications.

In addition, an Information Disclosure Statement is filed herewith.

REAL PARTY OF INTEREST

NanoGram Corp., a corporation organized under the laws of the state of Delaware, and having offices at 46774 Lakeview Boulevard, Fremont, CA 94538, has acquired the entire right, title and interest in and to the invention, the application, and any and all patents to be obtained therefor, as set forth in the Assignment

filed with the patent application and recorded on Reel 010372, frame 0078.

RELATED APPEALS AND INTERFERENCES

One of the parent applications of the present continuation-in-part application, U.S. Patent Application 09/136,483, is presently under appeal. However, Applicants do not believe that the outcomes of the appeals are related.

STATUS OF THE CLAIMS

All pending claims, claims 1-28 and 31, stand rejected.

STATUS OF AMENDMENTS

All amendments have been entered. A Response after final has been considered by the Examiner.

SUMMARY OF INVENTION

The present invention relates to the formation of dispersions of nanoparticles with average particle sizes less than about 50 nm. Dispersions are liquids in which the particles are dispersed through the liquid. A feature of the particles is that they have a distribution of primary particle sizes such that less than about 1 in one million (10^6) particle have a diameter greater than about three times the average particle diameter for the collection of particles. In other words, the particles are highly uniform in that the particles do not have a tail in the particle size distribution. The invention also covers methods of polishing surfaces with highly uniform particle dispersions.

The production of highly uniform particles is enabled by the use of laser pyrolysis. Unlike standard chemical reactions under equilibrium conditions, the light beam defines a reaction zone in which the reaction is driven to completion. See the specification, for example, at page 6, line 24 to page 7, line 11,

page 6, lines 16-27 and page 12, lines 12-23. The extreme amount of heat in the reaction zone tends to dissociate reactants within the reaction zone. The species then recombine to form the product compositions. The reaction is rapidly quenched as the particles leave the reaction zone. See page 24, lines 10-18. This quenching terminates further reaction and corresponding particle growth. Since the reaction zone is small and well defined, the product particles are correspondingly uniform.

Pending claim 1, is directed to dispersions of a particle collection having extremely high uniformity expressed through a cut off in the particle size distribution. In other words, the plot of particle diameters does not have a tail at large diameters. For further description of these uniform particle collections, see the specification, for example, at page 35, line 31 to page 38, line 18. Specifically, less than one particle in one million particles have a diameter more than three times the average diameter. In some embodiments, less than one particle in one million particles have a diameter more than two times the average diameter. Such dispersions can be used effectively in a variety of applications described in the specification.

Similarly, pending claim 24 is specifically directed to the narrow distribution of particles near the average particle diameter. This narrowness in the particle size distribution is expressed as a sharp drop in the distribution of particle sizes away from the average particle size. This narrow distribution about the average is independent from the lack of a tail in the distribution, although they both relate to the particle size distribution and uniformity of the powders. This feature of the invention is described in the specification, for example, from page 37, line 13 to page 38, line 2. Applicants have produced powders with a distribution of particle sizes that is both narrow near its peak and without a tail at larger distributions.

Other aspects of the invention relate to the polishing of surfaces. The highly uniform particle dispersions can be used advantageously for improve polishing of surfaces. For surfaces that include a plurality of different materials, the particles dispersions can be used to polish the surface to selectively remove one material at a high rate relative to another material. In preferred embodiments, one material is removed at a rate at least about five time faster than another material. See Applicants' specification, for example, from page 49, line 11 to page 50, line 13.

Furthermore, it has been observed that the highly uniform abrasive nanoscale powders applied as a dispersion result in a surprisingly high polishing rate. Specifically, they have a polishing rate that is more than a factor of two greater than the polishing rate with comparable micron sized particles. Thus, more dilute dispersions of particles can be used, which require less surface cleaning after polishing. See Applicants' specification, for example, at page 51, lines 12-34.

ISSUES

1. Whether claim 27 is indefinite under 35 U.S.C. §112, second paragraph?

2. Whether claims 1-28 and 31 are unpatentable over either 1) U.S. Patent 5,935,278 to Ishitobi et al. (the Ishitobi patent) alone or in view of U.S. Patent 6,001,730 to Farkas et al. (the Farkas patent), 2) U.S. Patent 5,759,917 to Grover et al. (the Grover patent) alone or in view of the Farkas patent, or 3) U.S. Patent 5,783,489 to Kaufman et al. (the Kaufman patent) alone or in view of the Farkas patent?

3. Whether claims 1-28 and 31 are unpatentable under 35 U.S.C. §103(a) over either 1) U.S. Patent 5,861,054 to Miyashita et al. (the Miyashita patent) in view of the Farkas patent, or 2) U.S.

Patent 5,264,010 to Brancaleoni et al. (the Brancaleoni patent) in view of the Farkas patent?

4. Whether claims 1-4, 7-28 and 31 are unpatentable under 35 U.S.C. §103(a) over either 1) U.S. Patent 5,891,205 to Picardi et al. (the Picardi patent) in view of the Ishitobi patent and the Farkas patent, 2) U.S. Patent 5,575,885 to Hirabayashi et al. (the Hirabayashi patent) in view of the Ishitobi patent and the Farkas patent, or 3) U.S. Patent 4,983,650 to Sasaki (the Sasaki patent) in view of the Ishitobi patent and the Farkas patent?

5. Whether claims 1-28 and 31 are unpatentable under 35 U.S.C. §103(a) over either 1) U.S. Patent 5,868,604 to Atsugi et al. (the Atsugi patent) in view of the Ishitobi patent and the Farkas patent, or 2) U.S. Patent 5,389,194 to Rostoker et al. (the Rostoker patent) in view of the Ishitobi patent and the Farkas patent?

6. Whether claims 1-4, 7-18, 23-28 and 31 are unpatentable under 35 U.S.C. §103(a) over U.S. Patent 5,622,525 to Haisma et al. (the Haisma patent) in view of the Ishitobi patent and the Farkas patent?

7. Whether claims 1-28 and 31 are unpatentable for obviousness-type double patenting over copending application 08/961,735 in view of the Ishitobi patent and the Farkas patent and over copending application 09/266,202 in view of the Ishitobi patent and the Farkas patent?

GROUPING OF CLAIMS

1. Claims 1-22, 25, 26 and 28 form a first group of claims directed to a particle dispersion with average primary particle diameters less than about 50 nm and less than about 1 in one million particles having a primary particle diameter greater than about three times the average primary particle diameter.

2. Claim 23 is in a second group of claims directed to a particle dispersion having less than one particle in a million

having a primary particle diameter greater than about two times the average particle diameter.

3. Claim 24 is in a third group of claims directed to a particle dispersion having a distribution of diameters of primary particles with at least about 95 percent of the primary particles having a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter as well as less than about 1 in one million particles having a primary particle diameter greater than about three times the average primary particle diameter.

4. Claim 27 is in a fourth group of claims directed to a method of polishing a surface involving a plurality of compositions and wherein the dispersion has a selective removal rate of one surface composition being at least about 5 times greater than the removal rate of another surface composition.

5. Claim 31 is in a fifth group of claims directed to a method of polishing a surface of a metal or metal composition having a polishing rate that is at least about a factor of two greater than the polishing rate with a dispersion having particles with an average diameter greater than a micron.

ARGUMENT

1. Rejections Under 35 U.S.C. §112, Second Paragraph

The Examiner rejected claim 27 under 35 U.S.C. §112, second paragraph, as being indefinite. In particular, the Examiner has indicated that the meaning of "plurality of compositions" is unclear. Applicants respectfully request reconsideration of the rejection based on the following comments.

"Determining whether a claim is definite requires an analysis of whether one skilled in the art would understand the bounds of the claim when read in light of the specification If the claims read in light of the specification reasonably apprise

those skilled in the art of the scope of invention, §112 demands no more." Personalized Media Communications LLC v. ITC, 48 USPQ2d 1880, 1888 (Fed. Cir. 1998), quoting Miles Lab., Inc. v. Shandon, Inc., 27 USPQ2d 1123, 1126 (Fed. Cir. 1993).

The Examiner has not indicated what possible ambiguity results from the term "plurality of compositions." Clearly this expression means more than one composition. Such structures are described in Applicants specification from page 49, line 30 to page 50, line 13. Applicants maintain that the claim is clear. Applicants respectfully request the withdrawal of the rejection of claim 27 under 35 U.S.C. §112, second paragraph, as being indefinite.

2. Rejections Under 35 U.S.C. §103(a)

The Examiner has rejected all the pending claims over the prior art. The specific rejections are analyzed in detail below. First, Applicants summarize the relevant case law on obviousness and present arguments based on the case law that are generally applicable to all of the rejections. Also, Applicants also rebut the Examiner's position on legal issues prior to analysis of the specific references. The prior art references cited against the claims are presented in Appendix B.

A. Relevant Legal Analysis

"In rejecting claims under 35 U.S.C. §103, the examiner bears the initial burden of presenting a prima facie case of obviousness. In re Rijckaert, 28 USPQ2d 1955, 1956 (Fed. Cir. 1993). "Only if that burden is met, does the burden of coming forward with evidence or argument shift to the applicant." Id. All claim limitations must be taught or suggested by the prior art. See MPEP 2143.03.

"The mere fact that a certain thing **may** result from a given set of circumstances is not enough to establish inherency." In re Rijckaert, 28 USPQ2d at 1957, citing In re Oelich, 212 USPQ 323, 326 (CCPA, 1981)(emphasis in original). "That which is

inherent is not necessarily known. Obviousness cannot be predicated on what is unknown." In re Rijckaert, 28 USPQ2d at 1957, citing In re Spormann, 150 USPQ 449, 452 (CCPA 1966). "Such a retrospective view of inherency is not a substitute for some teaching or suggestion supporting an obviousness rejection." In re Rijckaert, 28 USPQ2d at 1957. "While the Commissioner criticizes Rijckaert's arguments regarding the §103 rejection, the burden to rebut a rejection of obviousness does not arise until a prima facie case has been established." Id. The In re Rijckaert case has considerable significance to the fact situation of the present application.

The proposition is well established that the prior art only renders a composition of matter unpatentable to the extent that the prior art provides a means of obtaining the composition.

To the extent that anyone may draw an inference from the Von Bramer case that the mere printed conception or the mere printed contemplation which constitutes the designation of a 'compound' is sufficient to show that such a compound is old, regardless of whether the compound is involved in a 35 U.S.C. 102 or 35 U.S.C. 103 rejection, we totally disagree. ... We think, rather, that the true test of any prior art relied upon to show or suggest that a chemical compound is old, is whether the prior art is such as to place the disclosed 'compound' in the possession of the public.

In re Brown, 141 USPQ 245, 248-49 (CCPA 1964) (emphasis in original) (citations omitted). Similarly, see In re Hoeksema, 158 USPQ 596, 600 (CCPA 1968) (emphasis in original):

We are certain, however, that the invention as a whole is the claimed compound **and** a way to produce it, wherefore appellant's argument has substance. There has been no showing by the Patent Office in this record that the claimed compound can exist because there is no showing of a known or obvious way to manufacture it; hence, it seems to us that the 'invention as a whole,'

which section 103 demands that we consider, is not obvious from the prior art of record.

While there are valid reasons based on public policy as to why this defect in the prior art precludes a finding of obviousness under section 103, *In re Brown*, supra, its immediate significance in the present inquiry is that it poses yet **another difference** between the claimed invention and the prior art which **must** be considered in the context of section 103. So considered, we think the differences between appellant's **invention as a whole** and the prior art are such that the claimed invention would not be obvious within the contemplation of 35 U.S.C. 103.

The Federal Circuit has further emphasized these issues. "But to be prior art under section 102(b), a reference must be enabling. That is, it must put the claimed invention in the hands of one skilled in the art." *In re Sun*, 31 USPQ2d 1451, 1453 (Fed. Cir. 1993) (unpublished). Assertions in a prior art reference do not support an anticipation or obviousness rejection unless the references place the claimed invention in the hands of the public. *Beckman Instruments Inc. v. LKB Produkter AB*, 13 USPQ2d 1301, 1304 (Fed. Cir. 1989). "In order to render a claimed apparatus or method obvious, the prior art must enable one skilled in the art to make and use the apparatus or method." *Id.* While a reference is prior art for all that it teaches, references along with the knowledge of a person of ordinary skill in the art must be enabling to place the invention in the hands of the public. *In re Paulsen*, 31 USPQ2d 1671, 1675 (Fed. Cir. 1994). See also *In re Donohue*, 226 USPQ 619, 621 (Fed. Cir. 1985).

"To serve as an anticipation when the reference is silent about the asserted inherent characteristic, such gap in the reference may be filled with recourse to extrinsic evidence. Such evidence must make clear that the missing descriptive matter is **necessarily present** in the thing described in the reference, and that it would be so recognized by persons of ordinary skill." *Continental Can Co. USA Inc. v. Monsanto Co.*, 20 USPQ2d 1746, 1749 (Fed. Cir. 1991) (necessarily present). "Inherency, however may not

be established by probabilities or possibilities. The mere fact that a certain thing **may** result from a given set of circumstances is not sufficient." Id., quoting Hansgirk v. Kemmer, 40 USPQ 665, 667 (CCPA 1939) (emphasis in original).

The Examiner has noted that "a reference is good not only for what it teaches but also for what one of ordinary skill might reasonably infer from the teachings." However, "[t]o imbue one of ordinary skill in the art with knowledge of the invention in suit, when no prior art reference or references of record convey or suggest that knowledge, is to fall victim to the insidious effect of a hindsight syndrome wherein that which only the inventor taught is used against its teacher." W. L. Gore & Assocs., Inc. v. Garlock, Inc., 220 USPQ 303, 312-13 (Fed. Cir. 1983). "Skill in the art does not act as a bridge over gaps in the substantive presentation of an obviousness case, but instead supplies the primary guarantee of objectivity in the process." All-Site Corp. v. VSI International Inc., 50 USPQ2d 1161, 1171 (Fed. Cir. 1999) (emphasis added).

Claims covering a range of composition narrower than a broader range covered in the prior art are prima facie obvious over the prior art. In re Malagari, 182 USPQ 549, 553 (CCPA 1974). Similarly, claims covering ranges overlapping or touching upon ranges disclosed in the prior art are also prima facie obvious. Id. There is some support for the proposition that prior art disclosing ranges that overlap with claimed ranges anticipate the claims. Ex parte Lee, 31 USPQ2d 1105, 1107 (USPTO Bd. Pat. App. & Int. 1993) (an expanded seven member board). Applicants do not believe that these cases are relevant to any pending claims, as described further below, since the prior art does not disclose particle collections with overlapping uniformity, relating to the particle size distribution.

The present claims are directed to compositions of matter. Applicants believe that the In re Gross and In re Irani

cases discussed below are on point with respect to relevant legal criteria for establishing obviousness of compositions of matter that have compositional properties distinct from prior art compositions of matter. Other cases below provide further context for evaluating the patentability of compositions of matter.

The claimed aspects of the present invention are chemical/compositional properties that make the material a different composition of matter. In particular, Applicants' claimed compositions have several compositional features of particular relevance. First, the composition of matter is a dispersion including a collection of particles. Also, the particles have a specified range of average particle sizes. Average particle size is a chemical/compositional property similar to chemical formula or molecular weight of a polymer. Collections of particles with one average particle size are a different composition of matter and will have different physical properties from collections of particles with other average particle sizes.

Similarly, the distribution of particle sizes is another independent chemical/composition property of solid particles that is distinct from the average particle size. A particle collection with a particular particle size distribution is a different composition of matter and will have different physical properties from other collections of particles with different particle size distributions. Applicants have developed an approach using laser pyrolysis to produce the highly uniform powders/particles, which is the subject of the present claims.

It is long established that a composition of matter is indistinguishable from its properties. In re Papesch, 137 USPQ 43, 51 (CCPA 1963); In re Cescon, 177 USPQ 264, 266 (CCPA 1973). There are two types of properties, chemical/compositional properties and physical properties. The chemical/compositional properties of the composition of matter determine what the material is, while the physical properties relate to the interaction and behavior of the

composition of matter. Often unique or unexpected physical properties are used to establish the existence of an unobvious composition when chemical/compositional properties either are unknown or do not fully represent the unobviousness of the composition. However, discovery of a surprising or unexpected physical property does not necessarily control an obviousness determination, and all the evidence under the Graham factors must be considered. See, for example, Richardson-Vicks v. Upjohn Co., 44 USPQ2d 1181, 1187 (Fed. Cir. 1997).

Obviousness under 35 U.S.C. §103 must be evaluated by viewing the invention as a whole. In re Langer, 175 USPQ 169, 171 (CCPA 1972). "In effect, we consider the prior art 'as a whole' with the claimed subject matter 'as a whole.'" Id. This rule superseded other principles, and specifically, "homology should not be automatically equated with prima facie obviousness." Id. (emphasis added). "To give meaning to the language of 35 U.S.C. 103 which speaks to the subject matter 'as a whole,' we feel weight must be given the properties of a compound or composition of matter." In re Murch, 175 USPQ 89, 92 (CCPA 1972) (emphasis added). "It has long been our position that a compound and its properties are inseparable and that no property can be ignored in determining patentability over the prior art." In re Cescon, 177 USPQ at 266.

These issues regarding properties of compositions of matter were considered explicitly in the context of **chemical powders** in In re Grose, 201 USPQ 57 (CCPA 1979). The specific issue in the Grose case was the crystal structure of zeolites in a collection of zeolite particles. **Crystal structure, like particle size distribution or chemical formula, is a chemical/ compositional property of the composition of matter.** The zeolites in the Gross case were collections of particles, i.e., a powder. The relevant issues are well stated in In re Grose:

Though nonobviousness of appellants' process for preparing their claimed composition would not be determinative of nonobviousness of the composition, a

holding that the composition would have been nonobvious would require that the prior art fail to disclose or render obvious a process for preparing it.

[I]f the prior art of record fails to disclose or render obvious a method for making a claimed compound, at the time the invention was made, it may not be legally concluded that the compound itself is in the possession of the public. In this context, we say that the absence of a known or obvious process for making the claimed compounds overcomes a presumption that the compounds are obvious. ***

In re Hocksema, 55 CCPA 1493, 1500, 399 F.2d 269, 274, 158 USPQ 596, 601 (1968) (foot note omitted). Failure of the prior art to disclose or render obvious a method for making any composition of matter, whether a compound or a mixture of compounds like a zeolite, precludes a conclusion that the compound would have been obvious.

In re Grose, 201 USPQ at 63-64 (emphasis added). Applicants note that in In re Grose the zeolites had the same chemical formula as the prior art zeolites and only differed in crystal structure.

"No reason exists for applying the law relating to structural obviousness of those compounds which are homologs or isomers of each other to this case. When the PTO seeks to rely upon chemical theory, in establishing a prima facie case of obviousness, it must provide evidentiary support for the existence and meaning of that theory. In re Mills, 47 CCPA 1185, 1191, 281 F.2d 218, 223-224, 126 USPQ 513, 517 (1960)." In re Grose, 201 USPQ at 63 (emphasis added).

"One of the assumptions underlying a prima facie obviousness rejection based upon a structural relationship between compounds, such as adjacent homologs, is that a method disclosed for producing one would provide those skilled in the art with a method of producing the other. That assumption does not apply, however, to the present case." Id. (emphasis added). Thus, if the prior art does not teach a method for making the claimed composition, the claimed composition of matter is not prima facie

obvious. If the composition of matter is not prima facie obvious, there is no necessity to disclose unexpected results relating to physical properties.

Another CCPA case similarly ruled that an anhydrous crystalline form of a material was patentable over a non-crystalline form. In re Irani, 166 USPQ 24 (CCPA 1970). As stated in that case,

As stated above, even assuming that one skilled in the art could have predicted with reasonable certainty that crystalline anhydrous ATMP could be produced, we are not convinced by this record how this could be achieved. We note that neither the examiner nor the board has contended that a suitable process would have been obvious. The closest that either has come to such a contention is the examiner's statement based on the disclosure in the Irani patent, that, as it turns out, 'little modification of the Petrov *** process will produce a crystalline material.' Obviousness, however, must not be based on hindsight and a 'little modification' can be a most unobvious one.

In view of the foregoing, we need not consider appellants' arguments regarding the differences in properties between appellants and Petrov's forms of ATMP.

In re Irani, 166 USPQ at 27 (bold added). This case explicitly confirms that unexpected results do not need to be shown if there is no disclosure in the prior art of a method of producing the composition of matter.

B. Rebuttal of Examiner's Legal Positions

Except for the Rostoker patent, the Examiner admits in the Office Action of September 25, 2000 that the references do not "literally define" the claimed particle size distributions. The Rostoker patent is described below in detail. The Examiner notes that any collection of particles have a distribution of particle sizes. The Examiner has taken the position that the particle size distribution is "apparent." Then, the Examiner concludes that in total the references make the claimed distribution suggested or apparent.

It is not clear what the Examiner means by "apparent." Certainly, the references do not suggest the claimed narrow particles size distributions. Apart from Rostoker, discussed below, the Examiner has pointed to no language to indicate such a suggestion. The Examiner seems to be suggesting that the narrow particle size distributions are inherent. As the case law above makes clear, inherency cannot be based on probabilities or possibilities. See, *supra*, the discussion of Continental Can Co. USA Inc. and Hansgirk cases. This principle has been well established for at least 60 years.

The Examiner's position falls far short of establishing prima facie obviousness. The fact that all collections of particles have a distribution of particle sizes does not make all distributions obvious. As noted above, the distribution of particle sizes is a property that is independent of average particle size. All distributions are not obvious. While the Examiner asserts without any basis that the prior art generally suggests the claimed distributions, the case law summarized above is clear that the property must be suggested to a person of skill in the art viewing the references along with a method of making the powders with the claimed particle size distributions.

The case law is very clear that all properties of a composition of matter must be taken into account in evaluating patentability, including the present particle size distribution. See, In re Grose and In re Irani above. With respect to particle size distribution, which is independent of average particle size, the Examiner has not indicated what ranges are overlapping. Unless the Examiner can point to overlapping ranges relating to particle size distribution, independent of average particle size, In re Malagari just is not relevant. The relevant cases are In re Grose and In re Irani, above.

A collection of particles having a narrower particle size distribution is analogous to a more pure composition of matter. In

other words, a powder with a narrower particle size distribution corresponds to a more uniform material. Thus, relevant case law regarding purity of compositions of matter should be considered also.

"It seems to us that the answer to that question is self-evident: by definition, pure materials necessarily differ from less pure materials and, if the latter are the only ones existing and available as a standard of reference, as seems to be the case here, perforce the 'pure' materials are 'new' with respect to them." In re Bergstrom, 166 USPQ 256, 262 (CCPA 1970).

Thus, if a compound with a particular molecular formula cannot be made based on the teachings in the prior art, the compound is patentable if a method is discovered for making the compound. Similarly, a collection of particles is patentable if the prior art did not disclose a method of producing the collection of particles. In particular, if a collection of particles with a narrower distribution of particle sizes is discovered, this collection of particles is patentable over the prior art if the prior art did not disclose an obvious method of making the highly uniform particles.

The Examiner seems to assert that all particle size distributions overlap all other particle size distributions if they have overlapping average particle sizes. However, the particle size distribution is an **independent property** from the average particle size. Particle size distribution, like crystal structure of zeolites in the In re Grose case discussed above, is a compositional property of the composition of matter that defines the composition of matter. **The particle size distribution is independent of average particle size just as crystal structure of zeolites is different from their chemical formula in in re Grose.** The Examiner has suggested that Applicants demonstrate unexpected properties. However, the case law is crystal clear, see In re Grose and In re Irani above, that Applicants have no need to show

unexpected result relating to physical properties unless the prior art teaches a method of making Applicants' claimed composition of matter including all of its chemical/compositional properties.

Similarly, disclosing a new physical property will not make an old material patentable. Generally, physical properties are used to establish patentability when chemical/compositional properties are not known or measurable well enough to distinguish materials. Here, the chemical/compositional distinguishing features are known and claimed.

The Examiner strenuously argues that an unexpected property must be disclosed by Applicants. Such a property is already disclosed. The unexpected property is the absence of particles having a diameter more than three times the average particle diameter in combination with an average particle size less than about 50 nm. No further unexpected property is needed.

C. Rejections Over Ishitobi et al., Grover et al., Kaufman et al., and Farkas et al.

The Examiner rejected claims 1-28 and 31 under 35 U.S.C. §103(a) as being unpatentable over either 1) U.S. Patent 5,935,278 to Ishitobi et al. (the Ishitobi patent) alone or in view of U.S. Patent 6,001,730 to Farkas et al. (the Farkas patent), 2) U.S. Patent 5,759,917 to Grover et al. (the Grover patent) alone or in view of the Farkas patent, or 3) U.S. Patent 5,783,489 to Kaufman et al. (the Kaufman patent) alone or in view of the Farkas patent. The examiner cited the Ishitobi patent, the Farkas patent, the Grover patent and the Kaufman patent for disclosing polishing compositions with nanoscale particles. Applicants respectfully request reconsideration of the rejection of the claims based on the following comments.

The Examiner asserted that the cited references have overlapping ranges with the claims and that the claims are therefore prima facie obvious. The Examiner further asserts that selection of solvent is an obvious modification. In addition, the

Examiner asserts that particle size determines surface roughness so that polishing with the particles with a similar average particle size would result in the same surface roughness.

With respect to claims 1-28, the claims specify that less than 1 in 10^6 primary particles have a diameter greater than 3 times the average diameter. This is a characteristic of the dispersion that is not disclosed explicitly or inherently or with overlapping ranges in any of the cited references. With respect to overlapping ranges, the Examiner is evidently referring to the average particle size. However, all features of the claimed composition of matter must be rendered obvious by the prior art, not just one selected feature. The case law is perfectly clear that all properties of a composition of matter must be considered when evaluating patentability. See In re Cescon, supra. Furthermore, the polishing characteristics depend on the particle size distribution and not just the average particle size. Applicants do not believe that dispersions with the claimed characteristics are disclosed in or rendered obvious by any of the cited references.

Applicants have presented evidence that dispersions including silicon oxides or metal oxides generally have not been known with the claimed characteristics. To support this proposition, Applicants submitted with the Response of November 17, 2000 four relevant references that show particle size distributions for silicon oxide or metal oxide nanoparticles. These references are attached in Appendix C, below. With respect to fumed silica, Applicants refer to U.S. Patent 5,246,624 to Miller et al. (the Miller patent). The Miller patent describes the formation of colloidal dispersions with fumed silica. The formation of fumed silica is described at column 1, lines 26-44. As described at column 1, lines 33-36, initially formed particles fuse to form "chain-like aggregates." The aggregates have a range in size from 0.5 microns to 44 microns. Clearly, chain-like aggregates have a

broad distribution in particle sizes since aggregate growth is inherently less controlled than particle growth from a single nucleus.

An aqueous phase method for the formation of silicon oxide particles from a silica gel is described in U.S. Patent 5,158,758 to Chieng et al. (the Chieng patent). The materials have extremely small pore sizes, on the order of 5 nm to 20 nm (50 to 200 angstroms), see column 3, lines 16-20. When the materials were subsequently ground to form particles, the particles had micron scale diameters, see Example 3 and other examples of the Chieng patent. Furthermore, the particles have a very broad distribution in size, as shown in Table 4, relative to the very narrow distribution disclosed and claimed by Applicants.

An article by Schmidt et al., "Fabrication of Agglomerate-Free Nanopowders by Hydrothermal Chemical Processing," Mat. Res. Soc. Symposium Proc. 50:21-31 (1998), describes the production of silica and metal oxides by gel methods to produce particles with relatively narrow size distributions. Their secondary particle size distributions can be seen in Fig. 3b. Note that the particle size scale is a **log scale**, which inherently makes the distribution look much narrower than a linear scale. The distribution has an average of about 20 nm (0.02 microns) and there are particles with diameters of at least about 200 nm according to the plot. Thus, **the distribution is much broader than the particle distribution that is claimed by Applicants.**

In addition, Applicants refer to U.S. Patent 4,356,107 to Payne (the Payne patent). The Payne patent describes a specific approach to form silica particles with a narrow particle size distribution based on a heat treatment of a silica gel. As noted in the Payne patent, the silica particles formed directly by the sol gel method have a particle size distribution much broader than disclosed and claimed by Applicants. As disclosed in Example IV of the Payne patent, the resulting silica gel has a range of particle

sizes between 65 nm and 130 nm. Based on this indicated range, the average particle size is also between 65 nm and 130 nm. The Payne patent does not teach or suggest how to obtain different average particle sizes outside of this range. Applicants have amended claim 1 to indicate that the average particle size is less than about 50 nm.

With respect to the references cited by the Examiner, the Ishitobi patent discloses the use of zirconium oxide, aluminum oxide or silicon oxide to polish nickel-phosphorous discs. The zirconium oxide was produced by a sol method. The resulting particles had an average particle size of 50 nm. See column 7, lines 3-59. However, as discussed above, sol approaches inherently give a broad range of particle sizes that would fall well outside the claimed narrow particle size distribution ranges. Thus, the Ishitobi patent does not add any disclosure relevant to obtaining the narrow particles sizes claimed by Applicants in their dispersion.

The Grover patent discloses the use of conventional methods for the production of the abrasive particles for their polish. See, for example, from column 4, lines 30 to column 5, line 25. The abrasive particles described in the Grover patent do not have the extremely narrow particle size distributions disclosed and claimed by Applicants.

The Kaufman patent discloses polishes with abrasive particles. See, for example, column 4, lines 46-55. The particles are preferably nanoparticles produced by conventional methods. See, for example, column 4, lines 56-63 and column 5, lines 32-37. The Kaufman patent does not teach or suggest abrasive particles with the extremely narrow particle size distributions disclosed and claimed by Applicants.

Since the prior art does not teach or suggest how to produce particle dispersions with particles having the claimed

narrow primary particle size distribution, the cited prior art does not render obvious claim 1 or any claims depending from claim 1.

With respect to claims 23 and 24, these claims refer to even more uniform powders with additional limitations on the particle size distributions. The cited references are even more deficient with respect to teaching or suggesting these materials. With respect to claim 27, the cited references do not disclosed the claimed polishing properties.

With respect to claim 31, Applicants discovered that their highly uniform particles gave surprisingly high grinding rates. Applicants refer to Fig. 8 of U.S. Patent 5,861,054 to Miyashita et al. Generally, smaller particle sizes is associated with **slower grinding rates, not faster grinding rates**. Therefore, Applicants' observation was a surprising result. None of the cited references teach or suggest this observation.

In view of the above comments, Applicant believe that a prima facie showing of obviousness has not been established. **Applicants have presented clear evidence of the deficiencies of the references even though prima facie obviousness was not established.** Applicants have done more than whet is legally necessary to rebut the Examiner's position. Applicants respectfully request the withdrawal of the rejection of claims 1-32 under 35 U.S.C. §103(a) as being unpatentable over either 1) the Ishitobi patent alone or in view of the Farkas patent, 2) the Grover patent alone or in view of the Farkas patent, or 3) the Kaufman patent alone or in view of the Farkas patent.

D. Rejections Over Miyashita et al., Brancaleoni et al. and Farkas

The Examiner rejected claims 1-28 and 31 under 35 U.S.C. §103(a) as being unpatentable over either 1) U.S. Patent 5,861,054 to Miyashita et al. (the Miyashita patent) in view of the Farkas patent, or 2) U.S. Patent 5,264,010 to Brancaleoni et al. (the Brancaleoni patent) in view of the Farkas patent. The Examiner

cited the Miyashita patent and the Brancaleoni patent for disclosing dispersions with nanometer scale particles. Applicants respectfully request reconsideration of the rejections based on the following comments.

As noted above, the Farkas patent does not disclose how to produce nanoparticles with the extremely narrow primary particle size distribution disclosed and claimed by Applicants. The Miyashita patent does not disclose methods for the production of silicon nitride or other abrasive particles for use in their polishing slurry. Therefore, the Miyashita patent evidently relies on commercially available abrasive particles, such as silicon nitride, to produce the slurries. Since the Miyashita patent does not teach or suggest explicitly or inherently the production of particles with the very narrow particle size distributions disclosed and claimed by Applicants, the combined disclosures of the Miyashita patent and the Farkas patent do not render Applicants' claimed invention obvious.

The Brancaleoni patent discloses a polishing composition including cerium oxide, fumed silica and colloidal silica. See, for example, column 4, lines 34-37. The fumed silica and colloidal or precipitated silica are commercial materials. See, for example, column 3, lines 62-67 and column 4, lines 7-17. Similarly, the Brancaleoni patent describes the use of commercially available cerium oxide. See, for example, column 6, lines 60-63. The Brancaleoni patent does not teach or suggest explicitly or inherently the extremely narrow particle size distributions disclosed and claimed by Applicants. Therefore, the combined disclosures of the Brancaleoni patent and the Farkas patent do not render the claimed invention obvious.

Applicants respectfully request the withdrawal of the rejection of claims 1-32 under 35 U.S.C. §103(a) as being unpatentable over either 1) the Miyashita patent in view of the

Farkas patent, or 2) the Brancaleoni patent in view of the Farkas patent.

E. Picardi et al., Hirabayashi et al., Sasaki, Ishitobi et al. and Farkas et al.

The Examiner rejected claims 1-4 and 7-32 under 35 U.S.C. §103(a) as being unpatentable over either 1) U.S. Patent 5,891,205 to Picardi et al. (the Picardi patent) in view of the Ishitobi patent and the Farkas patent, 2) U.S. Patent 5,575,885 to Hirabayashi et al. (the Hirabayashi patent) in view of the Ishitobi patent and the Farkas patent, or 3) U.S. Patent 4,983,650 to Sasaki (the Sasaki patent) in view of the Ishitobi patent and the Farkas patent. The Examiner cited the Picardi patent, the Hirabayashi patent and the Sasaki patent for disclosing the use of nanoparticles for surface polishing. Applicants respectfully request reconsideration of the rejections over the Picardi patent, the Hirabayashi patent, the Sasaki patent, the Ishitobi patent and the Farkas patent in view of the following comments.

The cited references only disclose particles with overlapping average particle sizes. Applicants' claims also specify features of the particle size **distribution**. With respect to patentability, the prior art must teach how to produce the claimed materials with all of their structural features in order to render the claimed invention obvious. As noted above, the disclosures of the Ishitobi patent and the Farkas patent do not teach or suggest collections of particles with the extremely narrow primary particle size distribution claimed by Applicants.

The Picardi patent discloses polishing compositions formed from cerium oxide and silicon oxide. It is clear from a brief review of the photomicrographs in Figs. 1 and 2 of the Picardi patent that the distributions of particle sizes for the materials disclosed in the Picardi patent are much larger than the distributions claimed by Applicants. For example, in Fig. 1 there are many particles with very small diameters of 10 nm or less and

several particles visible with diameters on the order of 50 nm. In Fig. 2 of the Picardi patent, the distribution may even be broader with many small particles not being clearly resolved in the photo.

The main focus of the Hirabayashi patent is on acidic and oxidizing components of a polishing composition. The Hirabayashi patent does disclose the use of abrasive particles in the nanometer size range, for example, at column 4, lines 60-67. The Hirabayashi patent does not describe the production of the abrasive particles. Therefore, the Hirabayashi patent evidently refers to the use of commercially available abrasive particles. The Hirabayashi patent does not teach or suggest explicitly or inherently collections of particles with the extremely narrow particle size distributions disclosed and claimed by Applicants.

The Sasaki patent describes a polishing composition with amorphous silica. The Sasaki patent describes the use of either colloidal silica or silica powder. See column 2, lines 30-45. The Sasaki patent does not teach or suggest any nonconventional approaches for the production of silica particles. Thus, the Sasaki patent does not teach or suggest explicitly or inherently approaches to produce the particle dispersions disclosed and claimed by Applicants.

Since the Picardi patent, the Hirabayashi patent, the Sasaki patent, the Ishitobi patent and the Farkas patent are deficient with respect to disclosing collections of particles with the extremely narrow primary particle size distributions, the combined disclosures of these patents do not render Applicants' claimed invention obvious. Applicants respectfully request the withdrawal of the rejection of claims 1-4 and 7-32 under 35 U.S.C. §103(a) as being unpatentable over either 1) the Picardi patent in view of the Ishitobi patent and the Farkas patent, 2) the Hirabayashi patent in view of the Ishitobi patent and the Farkas patent, or 3) the Sasaki patent in view of the Ishitobi patent and the Farkas patent.

F. Atsugi et al., Rostoker et al., Ishitobi et al., and Farkas et al.

The Examiner rejected claims 1-32 under 35 U.S.C. §103(a) as being unpatentable over either 1) U.S. Patent 5,868,604 to Atsugi et al. (the Atsugi patent) in view of the Ishitobi patent and the Farkas patent, or 2) U.S. Patent 5,389,194 to Rostoker et al. (the Rostoker patent) in view of the Ishitobi patent and the Farkas patent. The Examiner cited the Ishitobi patent and the Rostoker patent for disclosing the use of abrasive particles with an average particle size in the nanometer scale. Applicants respectfully request reconsideration of the rejections based on the following comments.

The Atsugi patent does not disclose any particular method for the production of nanoscale aluminum oxide particles. Presumably, the aluminum oxide particles are obtained from commercial sources. The Atsugi patent does not teach or suggest explicitly or inherently collections of particles with the extremely narrow particle size distributions disclosed and claimed by Applicants. As noted above, the Ishitobi patent and the Farkas patent do not teach or suggest obtaining particles with the extremely narrow particle size distributions disclosed and claimed by Applicants. Therefore, the combined disclosures of the Atsugi patent, the Ishitobi patent and the Farkas patent do not render Applicants' claimed invention obvious.

The Rostoker patent does describe a particle size distribution, for example, at column 7, lines 4-26. Applicants have struggled to understand the precise meaning of the terms in the Rostoker patent with respect to their asserted distributions. If the Examiner can explain how the distributions described in the Rostoker patent fall within Applicants' claimed distributions, Applicants would appreciate such an explanation so that the issue can be directly addressed. Having failed in the attempt to relate the Rostoker distribution with Applicants' claimed distribution,

Applicants turned to the teachings of the Rostoker patent relating to the formation of aluminum oxide.

The Rostoker patent does not teach the formation of aluminum oxide and only includes prophetic examples. The Rostoker patent discloses only one approach for obtaining nanoparticles of Al_2O_3 , a process described in U.S. Patent 5,128,081 to Siegel et al. (the Siegel patent). The Siegel patent is attached in Appendix D. The Siegel patent describes the use of a gas phase condensation approach to producing the particles. This approach leads to a tail at larger particle sizes that brings the distribution outside of Applicants' claimed ranges. As evidence of this, Applicants previously filed a copy of a reference by Siegel et al., J. de Physique C5: Supplement 10 681-686 (October 1988). A copy of this article is presented in Appendix D. The inset in figure 1 shows a particle size distribution for titanium dioxide produced by the gas phase condensation approach. The discussion below figure 1 refers to the distribution as "typical of the particle-size distribution produced in the gas-condensation method."

The long tail at larger particle sizes in the distribution clearly distinguishes the materials from those claimed by Applicants. The average "grain size" is about 13 nm, and a significant fraction of the particles have a size larger than 160 percent of the average, i.e., about 21 nm. While the tail is truncated in the figure, it is clear from the presence of the tail shown in the histogram that more than 1 particle in one million will have a diameter greater than 39 nm, three times the average particle size. The elimination of larger particle sizes is critical for certain applications, such as polishing applications since larger particles can scratch the surface of the material being polished.

With respect to other availability of the aluminum oxide nanoparticles with a narrower size distribution, we note that Dr. Siegel was instrumental in the formation of Nanophase Technologies

Corporation (Nanophase). Nanophase was not able to scale up easily the gas-condensation approach described in the Siegel patent. Thus, a variation on the gas-condensation approach was developed, called Physical Vapor Synthesis Approach. While this new approach is suitable for the production of commercial quantities of powders, the particle size distributions for Physical Vapor Synthesis are considerably **broad**er than those obtained by the gas condensation approach. Applicants enclosed with an earlier amendment an advertisement article by Quinton Ford of Nanophase and pages downloaded from the Nanophase web site that confirm this conclusion. These are attached in Appendix D. Therefore, the nanoscale particles needed to form the dispersions claimed by Applicants' claim were not commercially available from Nanophase.

Applicants have not asserted that the Siegel patent is the only way to make aluminum oxide. However, Applicants submitted a declaration by one of the inventors in one parent case before the same Examiner. A copy of the Declaration is presented in Appendix E. The Kambe Declaration was submitted by Applicants as support that other approaches for the formation of Applicants' claimed invention are not available.

Applicants have addressed in the only ways that have been clear to them all of the issues raised by the Examiner. Applicants have been unable to ascertain any other suitable evidence to address the rejections. Specifically, the Rostoker patent describes no independent methods for producing alumina that Applicants can try to reproduce. While the Examiner has suggested a demonstration of unexpected results, Applicants are unsure what materials to directly compare against as appropriate proof of unexpected results. In addition, such unexpected results are legally unnecessary if there is no known or obvious method for producing Applicants' claimed composition of matter. Applicants have already demonstrated an unexpected result, namely the narrow particle size distribution claimed. Applicants maintain that the

rejections are legally insufficient and that the Examiner has failed factually to establish prima facie obviousness. To the extent that prima facie obviousness has been shown, Applicants have rebutted any evidence of obviousness as described above in this section.

Applicants do not dispute that the prior art discloses particles with corresponding average particle sizes. But the particle size distribution must be considered separately since it is an independent property. By analogy, if crystallinity is at issue, the stoichiometry of the composition is not determinative of patentability even though stoichiometry directly affects available crystal structures. See, In re Grose and In re Irani above. With respect to particle size distribution independent of average particle size, the Examiner has not indicated what ranges are overlapping. Unless the Examiner can point to overlapping ranges relating to particle size distribution, independent of average particle size, In re Malagari just is not relevant. The relevant cases are In re Grose and In re Irani, above.

A collection of particles having a narrower particle size distribution is analogous to a more pure composition of matter. In other words, a powder with a narrower particle size distribution corresponds to a more uniform material. Thus, relevant case law regarding purity of compositions of matter should be considered also.

Since the cited references do not disclose the particles with a extremely narrow primary particle size distribution as claimed by Applicants, the combined disclosures of the Rostoker patent, the Ishitobi patent and the Farkas patent do not render Applicants' claimed invention obvious.

Applicants respectfully request the withdrawal of the rejection of claims 1-32 under 35 U.S.C. §103(a) as being unpatentable over either 1) the Atsagi patent in view of the

Ishitobi patent and the Farkas patent, or 2) the Rostoker patent in view of the Ishitobi patent and the Farkas patent.

G. Haisma et al., Ishitobi et al., and Farkas et al.

The Examiner rejected claims 1-4, 7-18 and 23-32 under 35 U.S.C. §103(a) as being unpatentable over U.S. Patent 5,622,525 to Haisma et al. (the Haisma patent) in view of the Ishitobi patent and the Farkas patent. The Examiner cited the Haisma patent for disclosing the use of nanoscale silica in a dispersion. Applicants respectfully request reconsideration of the rejections based on the following comments.

The Haisma patent does not describe the production of silicon oxide particles. Therefore, the Haisma patent implicitly discloses the use of commercial silica. Thus, the Haisma patent does not teach or suggest explicitly or inherently the narrow primary particle size distributions disclosed and claimed by Applicants. As noted above, the Ishitobi patent and the Farkas patent do not teach or suggest explicitly or inherently obtaining particles with the extremely narrow particle size distributions disclosed and claimed by Applicants. Therefore, the combined disclosures of the Haisma patent, the Ishitobi patent and the Farkas patent do not render Applicants' claimed invention obvious.

Applicants respectfully request withdrawal of the rejection of claims 1-4, 7-18 and 23-32 under 35 U.S.C. §103(a) as being unpatentable over the Haisma patent in view of the Ishitobi patent and the Farkas patent.

3. Double Patenting Rejection

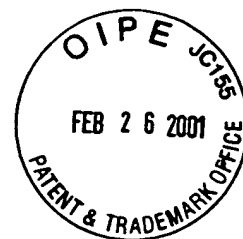
The Examiner provisionally rejected claims 1-32 under the judicially created doctrine of obviousness-type double patenting over either 1) all pending claims of copending Application No. 08/961,735 in view of the Ishitobi patent and the Farkas patent, 2) claims 9-15 of copending Application No. 09/085,514 in view of the Ishitobi patent and the Farkas patent, 3) claims 9-15 of copending Application No. 09/136,483 in view of the Ishitobi patent and the

Farkas patent, or 4) all the pending claims of copending Application No. 09/266,202 in view of the Ishitobi patent and the Farkas patent. Applicants have filed herewith a terminal disclaimer over copending Applications 09/085,514 and 09/136,483 to obviate the double patenting rejections over these two copending applications.

However, Applicants do not believe that any pending claims are obvious over the claims of copending Application No. 08/961,735 in view of the Ishitobi patent and the Farkas patent. In particular, the claims of Application No. 08/961,735 and the disclosures of the cited patents do not disclose collections of particles with less than 1 in one million particle having a diameter greater than about three times the average diameter. Similarly, Applicants do not believe that any claims of the present invention are obvious over any claims of copending Application No. 09/266,202 in view of the Ishitobi patent and the Farkas patent. In particular, none of the claims of Application No. 09/266,202 are directed to dispersions of particles.

The Examiner has again indicated that the claimed distributions are "apparent." This is an obviousness standard of which Applicants are unaware. The case law is clear that the prior art must teach the invention to a person of skill in the art. For a feature to be inherent, such a feature must be recognized by a person of skill in the art based on the prior art disclosure. The Examiner has failed to demonstrate that such a feature would be apparent to a person of skill in the art.

Since the claim of the copending applications along with the additional cited art do not teach or suggest the claimed invention, Applicants respectfully request withdrawal of the rejection of claims 1-32 under obviousness double patenting over 1) the claims of copending Application No. 08/961,735 in view of the Ishitobi patent and the Farkas patent and 2) the claims of



copending Application No. 09/266,202 in view of the Ishitobi patent and the Farkas patent.

CONCLUSIONS AND REQUEST FOR RELIEF

Applicants submit that claims 1-28 and 31 are unobvious over the prior art of record. Applicants believe that the Examiner has failed to establish prima facie unpatentability of any of the claims. To the extent that the Examiner has provided a prima facie showing of unpatentability, Applicants have provided adequate evidence to establish patentability over the issues of record. Thus, Applicants respectfully request the reversal of the rejections of claims 1-28 and 31 and the allowance of claims 1-28 and 31.

Respectfully submitted,

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PSD:nhw

Appendix A



PENDING CLAIMS

1. A particle dispersion comprising a liquid and a collection of particles at a concentration of less than about 50 weight percent in the dispersion, the collection of particles having an average primary particle diameter less than about 50 nm and less than about one in 10^6 particles having a primary particle diameter greater than about three times the average primary particle diameter.
2. The particle dispersion of claim 1 having an average secondary particle size less than about 1000 nm.
3. The particle dispersion of claim 1 wherein the particles comprise a compound selected from the group consisting of silicon nitride, silicon carbide, Al_2O_3 , CeO_2 , TiO_2 , MnO , ZnO , MnO_2 , Mn_2O_3 , Mn_3O_4 , SnO_2 , Fe_2O_3 , ZrO_2 , SiO_2 , alumina silicate, alumina titanate, carbon, and mixtures thereof.
4. The particle dispersion of claim 1 wherein the particles comprises a metal oxide.
5. The particle dispersion of claim 1 having a pH less than about 4 pH units.
6. The particle dispersion of claim 1 having a pH less than about 3 pH units.
7. The particle dispersion of claim 1 having a pH greater than about 9 pH units.
8. The particle dispersion of claim 1 having a pH from about 9 pH units to about 11 pH units.

9. The particle dispersion of claim 1 having a pH from about 6 pH units to about 8 pH units.
10. The particle dispersion of claim 1 further comprising a surfactant.
11. The particle dispersion of claim 10 wherein the surfactant is selected from the group consisting of octoxynol, nonxynol, and dodecyl trimethyl ammonium bromide.
12. The particle dispersion of claim 1 further comprising an oxidizing agent.
13. The particle dispersion of claim 12 wherein the oxidizing agent is selected from the group consisting of potassium ferricyanide, ~~potassium iodate~~ hydrogen peroxide, and ferric nitrate. *comma*
14. The particle dispersion of claim 1 wherein the liquid comprises water.
15. The particle dispersion of claim 1 wherein the liquid comprises an organic liquid.
16. The particle dispersion of claim 15 wherein the organic liquid is selected from the group consisting of alcohols, acetone, and carboxylic acids.
17. The particle dispersion of claim 1 wherein the liquid comprises a solution of water and an organic solvent.
18. The particle dispersion of claim 1 wherein the average primary particle diameter is from about 5 nm to about 50 nm.

19. The particle dispersion of claim 1 wherein the concentration of the collection of particles is less than about 30 weight percent.

20. The particle dispersion of claim 1 wherein the concentration of the collection of particles is less than about 20 weight percent.

21. The particle dispersion of claim 1 wherein the concentration of the collection of particles is less than about 10 weight percent.

22. The particle dispersion of claim 1 wherein the concentration of the collection of particles is less than about 5 weight percent.

23. The particle dispersion of claim 1 wherein the collection of particles has less than about one in 10^6 particles with a primary particle diameter greater than about two times the average primary particle diameter.

24. The particle dispersion of claim 1 wherein the collection of particles have a distribution of diameters of the primary particles such that at least about 95 percent of the primary particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

25. The particle dispersion of claim 1 wherein the particles are produced by laser pyrolysis.

26. A method of polishing a surface comprising abrading the surface with a dispersion of claim 1.

27. The method of claim 26 wherein the surface comprises a plurality of compositions and wherein the dispersion has a selective removal upon abrading of the surface with the removal rate of one surface composition being at least about 5 times greater than the removal rate of another surface composition.

28. A method for forming a particle dispersion, the method comprising mixing a collection of particles with a liquid, the collection of particles having an average primary particle diameter from about 5 nm to about 50 nm and less than about one in 10^6 particles having a primary particle diameter greater than about three times the average primary particle diameter.

31. A method for polishing a surface comprising metal or a metal compound, the method comprising:

abrading the surface with a particle dispersion, the particle dispersion comprising a collection of particle having an average primary particle diameter less than about 50 nm, abrading the surface results in removal of greater than about a factor of two more material from the surface per unit time than corresponding polishing with an equivalent concentration of particles having an equivalent composition and an



average particle diameter of greater than
about 1 micron.

APPENDIX F

1. Claims from copending Application 08/961,735.
2. Claims from copending Application 09/266,202.

Claims of Copending Application 08/961,735

1. A polishing composition comprising a dispersion of particles, the particles comprising metal compounds and having an average particle diameter from about 5 nm to about 50 nm and a distribution of diameters such that at least about 95 percent of the particles have a diameter greater than about 60 percent of the average diameter and less than about 140 percent of the average diameter.

2. The polishing composition of claim 1 wherein the particles are dispersed in an aqueous solution.

3. The polishing composition of claim 1 wherein the particles are dispersed in a nonaqueous solution.

4. The polishing composition of claim 1 wherein the particles comprise a composition selected from the group consisting of SiO_2 , SiC , TiO_2 , Fe_3C , Fe_7C_3 , Fe_2O_3 , Fe_3O_4 , MoS_2 , MoO_2 , WC , WO_3 and WS_2 .

6. A method of smoothing a surface comprising the step of polishing the surface with the polishing composition of claim 1.

7. The method of claim 6 wherein the polishing is performed with a polishing pad.

8. The method of claim 6 wherein the polishing is performed with a motorized polisher.

9. A polishing composition comprising a dispersion of particles, the particles comprising metal compounds with an average particle diameter from about 5 nm to about 200 nm and a single crystalline phase with a uniformity of at least about 90 percent by weight.

9. The polishing composition of claim 1 having a single crystalline phase with a uniformity of at least about 90 percent by weight.

10. The polishing composition of claim 9 wherein the particles comprise a composition selected from the group consisting of SiO_2 , SiC , TiO_2 , Fe_3C , Fe_7C_3 , Fe_2O_3 , Fe_3O_4 , MoS_2 , MoO_2 , WC , WO_3 and WS_2 .

12. The polishing composition of claim 9 wherein the particles have a single crystalline phase with a uniformity of at least about 95 percent by weight.

13. The polishing composition of claim 9 wherein the particles have a single crystalline phase with a purity of at least about 99 percent by weight.

14. The polishing composition of claim 9 wherein the particles have a single crystalline phase with a purity of at least about 99.9 percent by weight.

15. A polishing composition comprising a dispersion of particles, the particles comprising metal compounds or silicon compounds with an average particle diameter from about 5 nm to about 50 nm and effectively no particles with a diameter greater than about 5 times the average diameter.

16. A polishing composition comprising an aqueous dispersion of particles, the particles comprising metal carbides or metal sulfides and having an average particle diameter from about 5 nm to about 200 nm.

23. The polishing composition of claim 15 wherein the particles are dispersed in an aqueous solution.

25. The polishing composition of claim 16 wherein the particles have an average diameter from about 5 nm to about 100 nm.

26. The polishing composition of claim 16 wherein the dispersion includes from about 0.05 to about 5 percent by weight particles.

27. The polishing composition of claim 16 wherein the particles have an average diameter from about 5 nm to about 50 nm.

28. The polishing composition of claim 16 wherein effectively no particles have an diameter greater than about 5 times the average diameter.

29. The polishing composition of claim 16 wherein the metal carbides or metal sulfides comprise metal carbides.

30. The polishing composition of claim 29 wherein the metal carbides comprise Fe_3C , Fe_7C_3 or WC.

31. The polishing composition of claim 29 wherein the metal carbides comprise SiC.

32. The polishing composition of claim 16 wherein the metal carbides or metal sulfides comprise metal sulfides.

33. The polishing composition of claim 16 wherein the particles have a distribution of diameters such that at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

34. The polishing composition of claim 16 wherein the particles have a distribution of diameters such that at least about 95 percent of the particles have a diameter greater than about 60 percent of the average diameter and less than about 140 percent of the average diameter.

CLAIMS FROM COPENDING APPLICATION 09/266,202

1. A collection of particles in a powder comprising crystalline zinc oxide, the collection of particles having an average diameter less than about 95 nm and a distribution of particle sizes such that at least 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.
2. The collection of particles of claim 1 wherein the collection of particles have an average diameter from about 5 nm to about 50 nm.
3. The collection of particles of claim 1 wherein the collection of particles have an average diameter from about 5 nm to about 25 nm.
4. The collection of particles of claim 1 wherein effectively no particles have a diameter greater than about four times the average diameter of the collection of particles.
5. The collection of particles of claim 1 wherein effectively no particles have a diameter greater than about three times the average diameter of the collection of particles.
7. An electrical resistor component comprising the collection of particle of claim 1.
8. The electrical resistor component of claim 7 wherein the component is a varister.
9. The electrical resistor component of claim 8 wherein the varister has a non-linear voltage dependance.
25. The collection of particles of claim 1 wherein effectively no particles have a diameter greater than about two times the average diameter of the collection of particles.
26. The collection of particles of claim 1 wherein at least 95 percent of the particles have ratios of the dimension along the major axis to the dimension along the minor axis less than about 2.
27. The collection of particles of claim 1 wherein the zinc oxide has a stoichiometry of ZnO.
28. The collection of particles of claim 1 wherein the zinc oxide has a stoichiometry of ZnO₂.

29. The collection of particles of claim 1 wherein the zinc oxide has a Zincite crystal structure.
30. The electrical resistor component of claim 7 further comprising metal/silicon oxide particles selected from the group consisting of Bi_2O_3 , Sb_2O_3 , SiO_2 , Co_2O_3 , and MnO_2 .
31. A display device comprising the collection of particles of claim 1.
32. The display device of claim 31 wherein the display device comprises a cathode ray tube.
33. The display device of claim 31 wherein the display device comprises a flat panel display.
34. The display device of claim 33 wherein the flat panel display comprises a field emission device.
35. The display device of claim 33 wherein the flat panel display comprises an electroluminescent display.

Appendix B

Cited References

1. U.S. Patent 4,983,650 to Sasaki
2. U.S. Patent 5,264,010 to Brancaleoni
3. U.S. Patent 5,389,194 to Rostoker et al.
4. U.S. Patent 5,575,885 to Hirabayashi et al.
5. U.S. Patent 5,622,525 to Haisma et al.
6. U.S. Patent 5,759,917 to Grover et al.
7. U.S. Patent 5,783,489 to Kaufman
8. U.S. Patent 5,861,054 to Miyashita
9. U.S. Patent 5,868,604 to Atsugi et al.
10. U.S. Patent 5,891,205 to Picardi et al.
11. U.S. Patent 5,935,278 to Ishitobi et al.
12. U.S. Patent 6,001,730 to Farkas et al.



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Sasaki

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[54] FINE POLISHING COMPOSITION FOR WAFERS

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[56] References Cited

U.S. PATENT DOCUMENTS

4,260,396 4/1981 Glemza 51/298

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[57] ABSTRACT

A fine polishing composition for wafers, comprising water, particulate amorphous silica and a polysaccharide polymer graft-polymerized with acrylamide alone or together with at least one vinyl monomer selected from the group consisting of acrylic acid, methacrylic acid and styrenesulfonic acid, and adjusted with an alkaline substance to a pH of from 8 to 12.

8 Claims, No Drawings

FINE POLISHING COMPOSITION FOR WAFERS

The present invention relates to a polishing composition to smooth the surface of wafers which are widely used as supporting crystals for integrated circuits. More particularly, it relates to a fine polishing composition to smooth the surface of wafers to remove irregularities exceeding 10 μm .

Wafers widely used as supporting crystals for integrated circuits, are usually prepared by slicing an ingot of silicon or germanium crystal, and their surface is then polished to form a flat surface free from irregularities as far as possible before formation of integrated circuit thereon. If irregularities are present on the wafer surface, it is difficult to form a circuit pattern precisely and finely on the surface, and such irregularities tend to lead to non-uniformity of the electric characteristics of the wafers.

Heretofore, various polishing agents have been proposed to polish the surface of such wafers.

For example, U.S. Pat. No. 3,170,273 discloses a silica sol having a silica concentration of from 2 to 50% by weight and a silica gel having a silica concentration of from 2 to 100%, as polishing agents. U.S. Pat. No. 3,328,141 discloses that an alkaline compound is added to such polishing agents to adjust the pH to a level of from 10.5 to 12.5, whereby the polishing rate can be increased. However, the wafer surface polished with these polishing agents, still has irregularities of from 5 to 50 μm when observed by a differential interference microscope and thus is not fully satisfactory.

Japanese Examined Patent Publication No. 9910/1978 discloses a polishing agent comprising quartz, a silicate and a hexafluorosilicate, which further contains a monovalent alcohol having from 3 to 5 carbon atoms and a polyvinyl alcohol. However, no adequately satisfactorily polished surface can be obtained even with this polishing agent. Besides, such a polishing agent containing an alcohol has a difficulty in the storage stability for a long period of time.

Further, U.S. Pat. No. 4,260,396 discloses a polishing agent containing water-soluble carboxymethylene gum or xanthane gum. However, such a polishing agent has a drawback that it takes a long polishing time to obtain a smooth polished surface and requires a long period of time for so-called rinse polishing conducted after polishing while supplying washing water. Further, it has a drawback that microorganisms utilizing xanthane gum as a nutrient source are likely to grow in the polishing agent, whereby it is difficult to maintain the storage stability for a long period of time.

It is an object of the present invention to overcome such drawbacks inherent to the conventional polishing compositions and to accomplish the following objectives:

- (1) To provide a polishing agent which is, when used for polishing a wafer, capable of providing a polished surface having no irregularities observable even by a differential interference microscope.
- (2) To provide a polishing agent which requires only a short period of time for providing a smooth surface.
- (3) To provide a polishing agent which requires only a short period of time for rinse polishing.
- (4) To provide a polishing agent having good storage stability for a long period of time.

The present inventors have conducted extensive research to accomplish the above objectives and as a

result, have found it possible to accomplish such objectives by providing a composition having a polysaccharide polymer graft-polymerized with a certain specific vinyl monomer incorporated in a slurry containing particulate amorphous silica and having the pH adjusted to a specific range with an alkaline substance, or by providing a composition obtained by incorporating a certain specific water-soluble salt to the above composition. The present invention has been accomplished on the basis of these discoveries. According to a first aspect, the present invention provides a fine polishing composition for wafers, comprising water, particulate amorphous silica and a polysaccharide polymer graft-polymerized with acrylamide alone or together with at least one vinyl monomer selected from the group consisting of acrylic acid, methacrylic acid and styrenesulfonic acid, and adjusted with an alkaline substance to a pH of from 8 to 12.

According to a second aspect, the present invention provides a fine polishing composition for wafers, comprising water, particulate amorphous silica, a polysaccharide polymer graft-polymerized with acrylamide alone or together with at least one vinyl monomer selected from the group consisting of acrylic acid, methacrylic acid and styrenesulfonic acid, and a water-soluble salt, and adjusted with an alkaline substance to a pH of from 8 to 12.

Now, the present invention will be described in detail with reference to the preferred embodiments.

As the particulate amorphous silica to be used in the present invention, colloidal silica sol or silica powder may be mentioned. It may be used in the form of an aqueous slurry wherein colloidal silica sol or silica powder is suspended in water, or in such a form that is capable of forming a slurry when added to water.

Such particulate amorphous silica usually has an average particle size within a range of from 5 μm to 10 μm . If the average particle size is less than 5 μm , the proportion of the silicic acid monomer or oligomer in the particles tends to be large, and if such particles are used for polishing, the silicic monomer or oligomer tends to deposit in the form of silica on the wafer surface, such being undesirable. If the average particle size exceeds 10 μm , the wafer surface tends to be susceptible to scratching.

In the present invention, the average particle size means an average particle size of independent particles when such particles are present in a separated state without coagulation, or an average particle size of coagulates when particles are present in a coagulated state.

The content of the particulate amorphous silica in the fine polishing composition for wafers according to the present invention, is usually at least 0.1% by weight. If the content is too small, no adequate effects will be obtained.

In the present invention, as the polysaccharide polymer, gua gum or xanthane gum may, for example, be mentioned. Gua gum is meant for viscous galactomannan contained in the albumen of seeds of gua which is a leguminous plant, and xanthane gum is meant for a polymer polysaccharide obtained by pure cultivation and fermentation of *Xanthomonas campestris*.

The fine polishing composition for wafers according to the present invention, contains a graft-polymerized polysaccharide polymer obtained by graft-polymerizing to the above-mentioned polysaccharide polymer an acrylamide monomer or a comonomer mixture composed of an acrylamide monomer and at least one vinyl

monomer selected from the group consisting of acrylic acid, methacrylic acid and styrenesulfonic acid.

By the graft-polymerization of the acrylamide monomer alone or together with other specific vinyl monomer to the above-mentioned polysaccharide polymer, it is possible to obtain a graft-polymerized polysaccharide polymer having high resistance against biochemical decomposition due to microorganisms without sacrificing the water-solubility of the polysaccharide polymer. The graft polymerization reaction of the polysaccharide polymer with the acrylamide monomer alone or together with other specific vinyl monomer proceeds efficiently and is therefore advantageous from the industrial point of view.

Further, the polishing composition containing such a graft-polymerized polysaccharide polymer is far superior in drag reduction effect to the polishing composition containing the non-graft polymerized polysaccharide polymer. The drag reduction effect is an effect whereby a turbulent flow hardly takes place even under a condition where the Reynolds number of the fluid is high. The drag reduction effect of the polishing composition of the present invention is high. This means that even when used for polishing under high pressure, the polishing composition maintains laminar flow and hardly forms a turbulent flow.

Acrylamide may be graft-polymerized to the polysaccharide polymer in accordance with a method described in detail, for example, in *Journal of Applied Polymer Science* Vol. 30, 4013-4018 (1985) and ditto, Vol. 32, 6163-6176 (1986). For example, when acrylamide is graft-polymerized to gua gum or xanthane gum, from 1 mmol to 1 mol of acrylamide and from 1 μ mol to 10 mmol of a polymerization initiator are added per g of gua gum or xanthane gum to an aqueous solution containing from 0.01 to 2.0% by weight of gua gum or xanthane gum, and the mixture is reacted at a temperature of from 0° to 100° C. in air or in the presence of an inert gas. As the polymerization initiator, a cerium ion type radical is preferably employed. Further, gua gum or xanthane gum is preferably of high purity.

The graft-polymerization of the above vinyl monomer and acrylamide to the polysaccharide polymer may be conducted as follows.

For example, when the above-mentioned vinyl monomer and acrylamide are graft-polymerized to gua gum or xanthane gum, from 1 mmol to 1 mol of the above vinyl monomer, from 1 mmol to 1 mol of acrylamide and from 1 μ mol to 10 mmol of a polymerization initiator are added per g of gua gum or xanthane gum to an aqueous solution containing from 0.01 to 2.0% by weight of gua gum or xanthane gum, and the mixture is reacted at a temperature of from 0° to 100° C in air or in the presence of an inert gas. As the polymerization initiator, a cerium ion type radical is preferably employed as in the above-mentioned case. Further, gua gum and xanthane gum is preferably of high purity as in the above case.

The content of the graft-polymerized polysaccharide polymer in the fine polishing composition for wafers according to the present invention, is usually at least 1 ppm, preferably from 10 to 1,000 ppm. When a wafer is polished with the polishing composition having a graft-polymerized polysaccharide polymer content within this range, a laminar flow will be formed in the direction of polishing between the polishing cloth and the wafer surface, whereby the wafer surface can be made smoother. If the content is less than 1 ppm, such a lami-

nar flow tends to be hardly formed. On the other hand, if the content exceeds 1,000 ppm, a turbulent flow is likely to be formed, such being undesirable.

The fine polishing composition for wafers according to the present invention is adjusted with an alkaline substance to a pH of from 8 to 12, preferably from 9 to 10, to maintain the silica sol under a stabilized condition.

As the alkaline substance, an alkali metal hydroxide, an amine or ammonia may be used. As the alkali metal hydroxide, potassium hydroxide, sodium hydroxide, rubidium hydroxide or cesium hydroxide may be mentioned. Among them, potassium hydroxide and sodium hydroxide are preferred. The amine includes triethylamine, triethanolamine, monoethanolamine, diisopropylamine, ethylenediamine, tetraethylpentamine, triethylpentamine, diethylenetriamine and hexamethylenediamine. Among them, ethylenediamine is preferred.

According to the second aspect of the present invention, the fine polishing composition for wafers further contains a water soluble salt in addition to the above described components. The water soluble salt has a function to reduce the thickness of the hydrated layer on the surface of silica particles in the fine polishing composition in the form of a slurry, whereby the dynamic action of the silica particles over the wafer during polishing operation of the wafer with the polishing composition, will increase, the mechanical polishing ability will increase, and the polishing efficiency will be improved.

Specific examples of the water-soluble salt include compounds composed of various combinations of a cation selected from the group consisting of lithium ion, sodium ion, potassium ion, cesium ion and ammonium ion and an anion selected from the group consisting of fluorine ion, chlorine ion, bromine ion, iodine ion, sulfuric acid ion, nitric acid ion, perchloric acid ion, carbonic acid ion, formic acid ion, acetic acid ion, acrylic acid ion and oxalic acid ion. Such compounds may be used alone or in combination as a mixture of two or more. Among them, potassium chloride and potassium perchlorate are preferred which have a high ionization degree in the polishing composition in the form of a slurry and the cation of which has a large atomic radius.

The content of the water-soluble salt in the fine polishing composition for wafers according to the second aspect of the present invention, is usually at least 20 ppm. By the incorporation of the water-soluble salt, it is possible to reduce the thickness of the hydrated layer formed on the surface of silica particles. If the content is less than 20 ppm, no adequate effects can be obtained.

The present invention provides the following remarkable effects and its industrial value for practical application is very high.

(1) When a wafer is polished with the fine polishing composition of the present invention, the above-mentioned graft-polymerized polysaccharide polymer in the slurry composition improves the drag reduction effect so that a laminar flow is formed between the polishing cloth and the wafer, while suppressing the formation of a turbulent flow. Accordingly, the polished wafer surface presents a smooth flat polished surface with no irregularities to be observed even when inspected with a differential interference microscope.

(2) The fine polishing composition of the present invention has a good storage stability for a long period of time, since the polysaccharide polymer graft-polymerized with an acrylamide monomer alone or together with other specific vinyl monomer, has high resistance

against biochemical decomposition due to microorganisms.

(3) The fine polishing composition according to the second aspect of the present invention, provides not only the above-mentioned effects (1) and (2), but also a function to reduce the thickness of the hydrated layer on the surface of silica particles in the fine polishing composition in the form of a slurry, by virtue of the water-soluble salt, whereby the dynamic action of the silica particles on the wafer during the polishing operation of the wafer increases, and the mechanical polishing ability increases and the polishing efficiency is improved.

Now, the present invention will be described in further detail with reference to Examples and Comparative Examples. However, it should be understood that the present invention is by no means restricted by such specific Examples.

EXAMPLE A-1

(1) Preparation of gua gum graft-polymerized with acrylamide

Gua gum having a high molecular weight (Mayprodol 120, tradename, manufactured by Sansho K.K.) was dissolved in water to obtain a 0.5 wt % aqueous solution. This solution was purified by a filtration method and an alcohol extraction method in the following manner. Firstly, coarse impurities in the gua gum aqueous solution were removed by filtration by means of a mesh filter having a pore size of from 1 to 10 μm . Gua gum does not dissolve in an alcohol. Therefore, the gua gum aqueous solution was poured into an alcohol to elute alcohol-soluble impurities, and the precipitate was recovered. The precipitate was dried and dissolved again in water to obtain an aqueous gua gum solution having a predetermined concentration i.e. a 1 wt % gua gum aqueous solution in this Example.

To 1 liter of the 1 wt % aqueous solution thus obtained, 0.5 mol of acrylamide was added, and the mixture was stirred while bubbling nitrogen. To this mixture, 0.3 mmol of ammonium cerium nitrate was added as a polymerization initiator, and the mixture was reacted at room temperature for 24 hours under stirring to obtain gua gum graft-polymerized with acrylamide.

The graft polymerization reaction may be conducted under an atmosphere of air by adding the polymerization initiator solution in an excess amount of about 10 mmol, or may be conducted by stirring the mixture for about one hour and leaving it to stand still thereafter.

(2) Preparation of a polishing composition

The 1 wt % aqueous solution of gua gum graft-polymerized with acrylamide obtained by the process of step (1) was added by an amount of 200 ppm as gua gum to an aqueous colloidal silica solution containing 2% by weight of silica having an average particle size of 70 μm . To the aqueous solution thus obtained, dimethylamine was added in an amount of 0.6% by weight to adjust the pH to a level of from 9 to 10 to obtain a fine polishing composition for wafers.

(3) Storage test of the polishing composition

The polishing composition obtained in step (2) was stored. Periodically, this composition was permitted to flow under a pressure of 4 kg/cm^2 in a capillary tube having an inner diameter of 0.5 mm and a length of 50 cm, and the pressures at the inlet and the outlet of the capillary tube were measured to determine the period of time until the pressure loss increases to a level of 0.4

time beyond the pressure loss of water. The results are shown in Table 1.

(4) Fine polishing test of a wafer

By a polishing machine SPAW 36, manufactured by Speed Fam, a silicon wafer was polished supplying the above-mentioned polishing composition at a rate of 1 l/min and using a soft sweade type polishing cloth. The polishing pressure was 100 g/cm^2 , and the relative speed of the polishing cloth to the wafer was 1 m/sec. The temperature of the polishing cloth during the polishing operation was 40° C.

The necessary polishing time for making smooth surface of wafer was measured. The determination for smoothness was evaluated by the observation of the wafer surface during the polishing operation by means of a differential interference microscope. The results are shown in Table 1.

After the polishing by the polishing machine, rinse polishing was conducted while supplying water instead of the above polishing composition to remove silica and the polysaccharide polymer from the wafer surface. The time required for the rinse polishing was measured. The completion of the rinse polishing was determined by the observation of the wafer surface by means of a differential interference microscope. The results are shown in Table 1.

EXAMPLE A-2

(1) Preparation of xanthane gum graft-polymerized with acrylamide

Xanthane gum having a high molecular weight (Kelzan F, tradename, manufactured by Sansho K.K.) was dissolved in water to obtain a 0.5 wt % aqueous solution.

This solution was purified in the same manner as in Example A-1(1), and the graft-polymerization of acrylamide was conducted also in the same manner to obtain xanthane gum graft-polymerization with acrylamide.

(2) Preparation of a polishing composition

The 1 wt % aqueous solution of xanthane gum graft-polymerized with acrylamide obtained in step (1) was added by an amount of 200 ppm as xanthane gum to an aqueous colloidal silica solution containing 2% by weight of silica having an average particle size of 70 μm . To the aqueous solution thus obtained, dimethylamine was added by an amount of 0.6% by weight to adjust the pH to a level of from 9 to 10 to obtain a fine polishing composition for wafers.

(3) Storage test of the polishing composition

The evaluation was conducted in the same manner as in Example A-1(3). The results are shown in Table 1.

(4) Fine polishing test of a wafer

The test was conducted in the same manner as in Example A 1(4). The results are shown in Table 1.

COMPARATIVE EXAMPLE A 1

(1) Preparation of a polishing composition

A polishing composition was prepared in the same manner as in Example A-1 except that gua gum (Mayprodol 120, manufactured by Sansho K. K.) purified in the same manner as in Example A-1(1) was used instead of the gua gum graft-polymerized with acrylamide, in Example A-1 (2).

(2) Storage test of the polishing composition

The evaluation was conducted in the same manner as in Example A-1(3). The results are shown in Table 1.

(3) Fine polishing test of a wafer

The evaluation was conducted in the same manner as in Example A-1(4). The results are shown in Table 1.

COMPARATIVE EXAMPLE A-2

(1) Preparation of a polishing composition

A polishing composition was prepared in the same manner as in Example A-2 except that xanthane gum (Kelzan F, manufactured by Sansho K.K.) purified in the same manner as in Example A-2(1) was used instead of the xanthane gum graft-polymerized with acrylamide, in Example A-2(2).

(2) Storage test of the polishing composition

The evaluation was conducted in the same manner as in Example A-1(3). The results are shown in Table 1.

(3) Fine polishing test of a wafer

The evaluation was conducted in the same manner as in Example A-1(4). The results are shown in Table 1.

stored even for a short period of time and thus have poor storage stability.

4. When the polishing is conducted by using the polishing compositions of the Comparative Examples, the fine polishing time and the rinse polishing time are both longer than the corresponding times in the Examples of the present invention.

EXAMPLE B-1

(1) Preparation of gua gum graft-polymerized with acrylic acid and acrylamide

Gua gum having a high molecular weight (Mayprogett 120, tradename, Sansho K.K.) was dissolved in water to obtain a 0.5 wt % aqueous solution. This solution was purified by a filtration method and an alcohol extraction method in the following manner.

Firstly, coarse impurities in the gua gum aqueous

TABLE 1

Items	Examples		Comparative Examples	
	A-1	A-2	A-1	A-2
<u>Particulate amorphous silica</u>				
Type	Colloidal silica	Colloidal silica	Colloidal silica	Colloidal silica
Average particle size (m μ m)	70	70	70	70
Content (wt %) in the composition	2.0	2.0	2.0	2.0
<u>Polysaccharide polymer</u>				
Type	Gua gum	Xanthane gum	Gua gum	Xanthane gum
Graft monomer component	AM ^{*2}	AM ^{*2}	—	—
Content (ppm) in the composition ^{*1}	200	200	200	200
<u>Alkaline substance, pH</u>				
Type	Dimethyl-amine	Dimethyl-amine	Dimethyl-amine	Dimethyl-amine
pH of the composition	9-10	9-10	9-10	9-10
Storage test of the composition	More than 1 month	More than 1 month	Less than 1 week	Less than 1 week
Period of time until the pressure loss increases to a level of 0.4 time beyond that of water				
Fine polishing test of a wafer				
Polishing time (min) required to obtain a smooth surface	5	5	10	10
Rinse polishing time (min)	0.5	0.5	1	1

^{*1}The content is expressed by the concentration of gua gum (Example A-1) or xanthane gum (Example A-2).

^{*2}AM means acrylamide.

The followings are evident from Table 1:

1. The polishing compositions of the present invention do not lose the drag reduction effects even when stored for a long period of time and thus have excellent storage stability.

2. When the polishing is conducted by using the polishing compositions of the present invention, the fine polishing time is short, and the rinse polishing time is also short, and thus the polishing compositions of the present invention are excellent as polishing agents.

3. Whereas, the polishing compositions of the Comparative Examples lose the drag reduction effects when

solution were removed by filtration by means of a mesh filter having a pore size of from 1 to 10 μ m. Gua gum is not soluble in an alcohol. Therefore, the gua gum aqueous solution was poured into an alcohol to elute alcohol-soluble impurities, and the precipitate was recovered. This precipitate was dried and then dissolved again in water to obtain an aqueous gua gum solution having a predetermined concentration, i.e. a 1 wt % gua gum aqueous solution in this Example.

To 1 liter of the 1 wt % aqueous solution thus obtained, 0.5 mol of acrylamide and 0.05 mol of acrylic acid were added, and the mixture was stirred while bubbling nitrogen. To this mixture, 0.3 mmol of ammo-

nium cerium nitrate was added as a polymerization initiator. The mixture was reacted at room temperature for 24 hours under stirring to obtain gua gum graft-polymerized with acrylamide and acrylic acid.

(2) Preparation of a polishing composition

The 1 wt % aqueous solution of gua gum graft-polymerized with acrylamide and acrylic acid obtained by the process of step (1), was added in an amount of 75 ppm as gua gum to an aqueous colloidal silica solution containing 0.7% by weight of silica having an average particle size of 70 μm . To the aqueous solution thus obtained, ammonia was added in an amount of 0.06% by weight to adjust the pH to a level of from 9 to 10 to obtain a fine polishing composition for wafers.

(3) Storage test of the polishing composition

The composition obtained in step (2) was stored at room temperature and periodically evaluated in the same manner as in Example A-1(3). The results are shown in Table 2.

(4) Fine polishing test of a wafer

The evaluation was conducted in the same manner as in Example A-1(4) except that the relative speed of the polishing cloth to the wafer was changed to 1.4 m/sec. The results are shown in Table 2.

EXAMPLE B-2

(1) preparation of gua gum graft-polymerized with methacrylic acid and acrylamide

Gua gum having a high molecular weight (Mayprogett 120, tradename, manufactured by Sansho K. K.) was dissolved in water to obtain a 0.5 wt % aqueous solution. This solution was purified in the same manner as in Example B-1(1) and dissolved in water to obtain a 1 wt % gua gum aqueous solution. To 1 liter of the 1 wt % aqueous solution thus obtained, 0.5 mol of acrylamide and 0.05 mol of methacrylic acid were added, and the mixture was stirred while bubbling nitrogen. To this mixture, 0.3 mmol of ammonium cerium nitrate was added as a polymerization initiator. The mixture was reacted at room temperature for 24 hours under stirring to obtain gua gum graft-polymerized with acrylamide and methacrylic acid.

(2) Preparation of a polishing composition

The 1 wt % aqueous solution of gua gum graft-polymerized with acrylamide and methacrylic acid obtained in step (1), was added by an amount of 75 ppm as gua gum to an aqueous colloidal silica solution containing 0.7% of silica having an average particle size of 70 μm . To the aqueous solution thus obtained, ammonia was added in an amount of 0.06% by weight to adjust the pH to a level of from 9 to 10 to obtain a fine polishing composition for wafers.

(3) Storage test of the polishing composition

The evaluation was conducted in the same manner as in Example A1(3). The results are shown in Table 2.

(4) Fine polishing test of a wafer

The evaluation was conducted in the same manner as in Example B-1(4). The results are shown in Table 2.

COMPARATIVE EXAMPLE B 1

(1) Preparation of a polishing composition

A polishing composition was prepared in the same manner as in Example B-1(2) except that gua gum purified in the same manner as in Example B-1(1) i.e. non-grafted gua gum, was used instead of the gua gum graft-polymerized with acrylamide and acrylic acid, in Example B-1(2), the amount of the gua gum was changed to 200 ppm and the content of silica was changed to 2% by weight.

(2) Storage test of the polishing composition

The evaluation was conducted in the same as in Example B-1(3). The results are shown in Table 2.

(3) Fine polishing test of a wafer

The evaluation was conducted in the same manner as in Example B-1(4). The results are shown in Table 2.

COMPARATIVE EXAMPLE B-2

(1) Preparation of a polishing composition

A polishing composition was prepared in the same manner as in Example B-1(2) except that gua gum purified in the same manner as in Example B-1(1) i.e. non-grafted gua gum, was used instead of the gua gum graft-polymerized with acrylamide and acrylic acid in Example B-1(2), the amount of the gua gum was changed to 75 ppm, and the content of silica was changed to 2% by weight.

(2) Storage test of the polishing composition

The evaluation was conducted in the same manner as in Example B-1(3). The results are shown in Table 2.

(3) Fine polishing test of a wafer

The evaluation was conducted in the same manner as in Example A-1(4). The results are shown in Table 2.

COMPARATIVE EXAMPLE B-3

(1) Preparation of a polishing composition

A polishing composition was prepared in the same manner as in Example B-1(2) except that gua gum purified in the same manner as in Example B-1(1) i.e. non-grafted gua gum, was used instead of the gua gum graft-polymerized with acrylamide and acrylic acid in Example B-1(2), the amount of gua gum was changed to 200 ppm, and the content of silica was changed to 0.7% by weight.

(2) Storage test of the polishing composition

The evaluation was conducted in the same manner as in Example B-1(3). The results are shown in Table 2.

(3) Fine polishing test of a wafer

The evaluation was conducted in the same manner as in Example A-1(4). The results are shown in Table 2.

TABLE 2

Items	Examples		Comparative Examples		
	B-1	B-2	B-1	B-2	B-3
Particulate amorphous silica					
Type	Colloidal silica	Colloidal silica	Colloidal silica	Colloidal silica	Colloidal silica
Average particle size (μm)	70	70	70	70	70
Content (wt %) in the composition	0.7	0.7	0.7	2.0	0.7
Polysaccharide polymer					

TABLE 2-continued

Items	Examples		Comparative Examples		
	B-1	B-2	B-1	B-2	B-3
Type	Gua gum	Gua gum	Gua gum	Gua gum	Gua gum
Graft monomer component	AM/AA ⁴	AM/MA ⁵	—	—	—
Content (ppm) in the composition ³	75	75	75	75	200
Alkaline substance, pH					
Type	Ammonia	Ammonia	Ammonia	Ammonia	Ammonia
pH of the composition	9-10	9-10	9-10	9-10	9-10
Storage test of the composition	More than 1 month	More than 1 month	Less than 1 week	Less than 1 day	Less than 1 week
Period of time until the pressure loss increases to a level of 0.4 time beyond that of water					
Fine polishing test of a wafer	4	4	10	No smooth surface obtained even by polishing for 20 minutes	
Polishing time (min) required to obtain a smooth surface					

³The content is expressed by the concentration of gua gum.

⁴AA means acrylic acid.

⁵MA means methacrylic acid.

⁶The content is expressed by the concentration of gua gum.

The followings are evident from Table 2:

1. The polishing compositions of the present invention do not lose the drag reduction effects even when stored for a long period of time and thus have excellent storage stability. 30

2. When the polishing is conducted by using the polishing compositions of the present invention, the fine polishing time is short. Thus, the polishing compositions of the present invention are suitable as polishing agents. 35

3. The silica content and the polymer content in the slurry required to accomplish the fine polishing can be small, such being economical.

4. Whereas, the polishing compositions of the Comparative Examples lose the drag reduction effects when stored even for a short period of time and thus have poor storage stability. 40

5. When the polishing is conducted by using the polishing compositions of the Comparative Examples, the silica content and the polymer content in the slurry required to accomplish the fine polishing are obliged to be larger than the Examples of the present invention, such being economically disadvantageous. 45

EXAMPLES C-1 TO C-4 and COMPARATIVE EXAMPLE C-1

To the fine polishing composition for wafers prepared in the same manner as in Example A-1(2) and to

the fine polishing composition for wafers prepared in the same manner as in Example B-1(2), a water-soluble salt was, respectively, added by the amount as shown in Table 3.

With respect to the fine polishing compositions for wafers thus obtained, the polishing tests of wafers were conducted in the same manner as in Example A-1(4) except that the relative speed of the polishing cloth to the wafer was changed to 1.2 m/sec.

Further, with respect to these fine polishing slurry compositions for wafers, the dispersion tests of the silica particles in the fine polishing compositions were conducted as follows.

The fine polishing slurry composition was put into a test tube having a height of 5 cm and a capacity of 100 cc and equipped with a stopper and left to stand still for one day. Then, the test tube was turned upside down and then to a normal position repeatedly until the silica particles were uniformly dispersed in the slurry as visually observed. The dispersibility was evaluated by the number of times of the operation until the uniform dispersion was obtained. The results are shown in Table 3.

TABLE 3

Items	Examples				Comparative Example C-1
	C-1	C-2	C-3	C-4	
Particulate amorphous silica					
Type	Colloidal silica	Colloidal silica	Colloidal silica	Colloidal silica	Colloidal silica
Average particle size (μm)	70	70	70	70	70
Content (wt %) in the composition	2.0	2.0	2.0	2.0	2.0
Polysaccharide polymer					
Type	Gua gum	Gua gum	Gua gum	Gua gum	Gua gum

TABLE 3-continued

Items	Examples				Comparative Example C-1
	C-1	C-2	C-3	C-4	
Graft monomer component	AM ^{*7}	AM	AM/AA ^{*8}	AM/AA	—
Process for preparation (Example)	A-1	A-1	B-1	B-1	—
Content (ppm) in the composition ^{*6}	200	200	75	75	—
Alkaline substance, pH					
Type	Dimethyl amine 9-10	Dimethyl amine 9-10	Dimethyl amine 9-10	Dimethyl amine 9-10	Dimethyl amine 9-10
pH of the composition					
Water-soluble salt					
Type	KCl	KCl	KCl	KCl	—
Content (wt %) in the composition	0.01	0.1	0.01	0.1	—
Fine polishing test of a wafer	3	1	3	1	More than 20
Polishing time (min) required to obtain a smooth surface					
Test for dispersibility of silica particles in the composition (times)			5		100

^{*6}The content is expressed by the concentration of gus gum.

^{*7}AM means acrylamide.

^{*8}AA means acrylic acid.

From Table 3, it is evident that the fine polishing compositions according to the second aspect of the present invention, the dispersibility of silica in the compositions is excellent.

I claim:

1. An aqueous based, slurried, fine polishing composition for wafers, comprising:

a water medium containing at least 0.1% by weight particulate amorphous silica having an average particle size within the range of from 5 μm to 10 μm and a polysaccharide polymer graft-polymerized with acrylamide alone or together with at least one vinyl monomer selected from the group consisting of acrylic acid, methacrylic acid and styrenesulfonic acid in a concentration of from 1 ppm to 1000 ppm, said aqueous composition being adjusted with an alkaline substance to a pH of from 8 to 12.

2. An aqueous based, fine polishing composition for wafers, comprising:

a water medium containing at least 0.1% by weight particulate amorphous silica having an average particle size within the range of from 5 μm to 10 μm and a polysaccharide polymer graft-polymerized with acrylamide alone or together with at least one vinyl monomer selected from the group consisting of acrylic acid, methacrylic acid and styrenesulfonic acid in a concentration of from 1 ppm to 1000 ppm, and a water-soluble salt, said aqueous

composition being adjusted with an alkaline substance to a pH of from 8 to 12.

3. The fine polishing composition according to claim 2, wherein the amount of said water-soluble salt is at least 20 ppm in the aqueous medium.

4. The fine polishing composition according to claim 1, wherein the amount of said particulate amorphous silica is 2 wt %.

5. The fine polishing composition according to claim 1, wherein the maximum amount of said particulate amorphous silica is an amount which still maintains a slurry.

6. The fine polishing composition according to claim 1, wherein the polysaccharide polymer is at least one member selected from the group consisting of water-soluble gus gum and xanthane gum.

7. The fine polishing composition according to claim 1, wherein the alkaline substance is an alkali metal hydroxide, an amine or ammonia.

8. The fine polishing composition according to claim 2, wherein the water-soluble salt is at least one compound composed of a combination of a cation selected from the group consisting of lithium ion, sodium ion, potassium ion, cesium ion and ammonium ion and an anion selected from the group consisting of fluorine ion, chlorine ion, bromine ion, iodine ion, sulfuric acid ion, nitric acid ion, perchloric acid ion, carbonic acid ion, formic acid ion, acetic acid ion, acrylic acid ion and oxalic acid ion.

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US005264010A

United States Patent [19]

Brancaleoni et al.

[11] **Patent Number:** 5,264,010[45] **Date of Patent:** Nov. 23, 1993[54] **COMPOSITIONS AND METHODS FOR
POLISHING AND PLANARIZING
SURFACES**[75] **Inventors:** Gregory Brancaleoni, Newark; Elmer W. Jensen, New Castle; John V. H. Roberts, Newark, all of Del.[73] **Assignee:** Rodel, Inc., Newark, Del.[21] **Appl. No.:** 874,654[22] **Filed:** Apr. 27, 1992[51] **Int. Cl.⁵** C09C 1/68[52] **U.S. Cl.** 51/308; 51/293;

51/309; 106/3; 106/6

[58] **Field of Search** 51/293, 308, 309;
106/3, 6[56] **References Cited****U.S. PATENT DOCUMENTS**

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Primary Examiner—Mark L. Bell*Assistant Examiner*—Willie J. Thompson*Attorney, Agent, or Firm*—Panitch, Schwarze, Jacobs & Nadel[57] **ABSTRACT**

An abrasive composition for use in polishing or planarizing the surface of a work piece is provided comprising about 30 to 50 percent of cerium oxide; about 8 to about 20 percent of fumed silica and about 15 to about 45 percent of precipitated silica. Methods using the composition to polish or planarize the surfaces of work pieces, as well as products produced by such methods, are also provided.

24 Claims, No Drawings

COMPOSITIONS AND METHODS FOR POLISHING AND PLANARIZING SURFACES

FIELD OF THE INVENTION

The present invention is directed to compositions useful for polishing and planarizing the surfaces of various work pieces, such as the surfaces of semiconductors, as well as methods for their use and products produced thereby.

BACKGROUND OF THE INVENTION

Compositions useful for polishing the surfaces of various work pieces are well known in the art. Conventional polishing compositions, which are used for polishing the surfaces of semiconductors, glass, crystal, metal and ceramic work pieces, generally comprise aqueous slurries of an appropriate abrasive agent or mixtures of such agents. Known abrasive agents include cerium oxide, aluminum oxide, zirconium oxide, tin oxide, silicon dioxide, titanium oxide, etc. Composition comprising such agents are generally used by first applying the composition to a polishing pad or to the surface to be polished. The polishing pad is then applied to the surface, which causes the abrasive particles contained within the composition to mechanically abrade the surface, thus effecting the polishing action. However, such conventional polishing compositions cannot produce the highly specular and planar surfaces required in semiconductor and microelectronic component technology. Moreover, conventional polishing compositions have demonstrated disadvantages, such as poor polishing rates and poor surface quality, in polishing other work pieces. For example, the surfaces of glass, metals, semiconductors, etc., polished with such compositions demonstrate various defects such as haze, stains, scratches, "orange peel", undulations, undercuts, mesas, etc.

Thus, attempts have been made to improve the efficiency and quality of polishing compositions. Two methods of attaining improvement in these areas have been directed to combining various abrasives and/or adding various adjuvants to the compositions.

Polishing compositions comprising specific combinations of abrasive particles are disclosed, e.g., in U.S. Pat. No. 4,601,755 which discloses polishing compositions comprising at least one crystalline phase of cerium oxide and a rare earth pyrosilicate. U.S. Pat. No. 4,786,325 discloses a glass polishing composition comprising ceric oxide and at least one oxide of a lanthanide or yttrium rare earth. Likewise, U.S. Pat. No. 4,769,073 discloses cerium-based polishing compositions for polishing organic glass surfaces which comprise ceric oxide, a cerous salt and optionally, pyrosilicates or silica.

Examples of the use of adjuvants in polishing compositions are disclosed, e.g., in U.S. Pat. No. 4,959,113 which discloses compositions useful for polishing metal surfaces which comprise water, an abrasive agent and a salt or a combination of salts to promote the polishing effectiveness of the metal surface by the abrasive agent. Similarly, U.S. Pat. No. 4,462,188 is directed to semiconductor polishing compositions which comprise a colloidal silica sol or gel, a water soluble amine and a water soluble quaternary ammonium salt or base. U.S. Pat. No. 4,588,421 discloses compositions useful for polishing silicon wafers comprising an aqueous colloidal silica solution gel and piperazine. It is disclosed that the addition of piperazine provides increased polishing

efficiency among other benefits. U.S. Pat. No. 4,954,142 discloses methods for polishing electronic components comprising contacting the surface of the component with a slurry comprising abrasive particles, a transition metal chelated salt and a solvent. This patent further discloses that the abrasive particles may be any of those commonly used such as silica, ceria, alumina, silicon carbide, silicon nitride, ferric oxide, etc.

However, even with such combinations of abrasive agents and the addition of adjuvant materials, conventional polishing compositions cannot produce the planarized surfaces needed in modern semiconductor and microelectronics technology.

Preparation of semiconductors and other microelectronic components generally involves building many interconnected layers of components, which may include products like very large scale integrated circuits (VLSIC) and ultra large scale integrated circuits (ULSIC). Thus, compositions useful for polishing or planarizing semiconductors must be able to polish complex, anisotropic, composite surfaces which are comprised of multiple layers of interconnected high density integrated circuits both at and below the surface. In preparing semiconductors, the structure resulting from the interconnected layers of integrated circuitry is polished down to a predetermined planar level which may comprise components of varying size, shape and hardness, as well as trenches, holes and valleys of various depths and shapes. After such polishing, semiconductor preparation may continue by various other procedures, such as chemical vapor deposition, metalization via vapor deposition, photolithographic patterning, diffusion, etching, etc., as will be recognized by one skilled in the art.

To provide superior results, the composition used to polish or planarize the surface of the prepared semiconductor work piece must produce an extremely flat and level surface with a high quality polish, i.e., a planar surface. However, unlike conventional polishing, to provide a planar surface, the polishing action must be restricted to the level surface of the work piece and must not affect the topography, morphology and/or structures below that surface. Only such selective polishing action will produce the desired planar surface. Conventional polishing compositions are not suited for such procedures as they merely produce uneven, undulating surfaces by abrading certain regions on, below and within the surface of the work piece. It has proven difficult, if not impossible, to use conventional polishing products to obtain smooth defect-free surfaces wherein the polishing composition does not adversely effect the underlying structure of the work piece.

In these specialized fields of semiconductor and microelectronic component preparation, where layers of components are interconnected within tiny chips of silicon, ceramic or other insulator work pieces, extraordinarily planar surfaces are required at many levels. Otherwise, the function of the semiconductor or other device may be adversely affected to the point where it is worthless. Thus, the many microprocessing steps used to make such a device and the associated labor and equipment may be wasted by only one surface which may be defective because planarization techniques did not produce sufficiently planar surfaces.

Accordingly, it can be seen that there has been a long-felt need for compositions which provide improved polishing activity at improved rates, which will

pounds or mixtures of surfactant compounds. The surfactant compounds act as suspension agents, thus aiding in the preparation of the present compositions. The addition of the surfactant acts to allow the aqueous slurries containing the present abrasive composition to take the form of a thixotropic composition. Moreover, it is believed that the surfactant compounds may provide an "anti-scratching" effect on the surface of the work piece being polished or planarized, thereby further decreasing the extent of surface defects caused by the abrasive agents.

The surfactant compounds may be present in the aqueous slurries in an amount of about 0.01 to about 2.0 percent and preferably about 0.015 to about 0.15 percent based on the weight of the slurry composition. Suitable surfactant compounds include any of numerous non-ionic, anionic, cationic or amphoteric surfactants known to those skilled in the art. The use of appropriate surfactants for a particular application will be evident to one of ordinary skill in the art based upon the present disclosure. However, it is preferred that octylphenylethyleneoxide, nonylphenylethyleneoxide, octylphenoxypolyethoxyethanol, polyoxyethylene (10) octylphenol ether, nonyl phenol polyether, polyoxyethylene (20) sorbitan monooleate, poly(oxy-1,2-ethanediyl)alpha-(nonylphenyl)omega-hydroxy, aliphatic ethoxylates, salts of carboxylic acid polyamine amides, alkylammonium salts of polymers having anionic or ionic character, polycarboxylic acids, acrylic acid copolymers or mixtures thereof, be used as the surfactant. Most preferably, the nonionic surfactant, octylphenoxypolyethoxyethanol is used as the surfactant in the present compositions. This surfactant is commercially available as "TRITON® X-102" from Rohm and Haas Co.

Generally, the aqueous slurries of the present compositions should be maintained at a pH of about 4 to about 12 and preferably at a pH of about 6 to about 11.4. In order to maintain the pH within the desired ranges, the present compositions may further comprise an appropriate acidic or basic substance in an amount appropriate to maintain the desired pH. Examples of suitable acidic and basic substances which may be used in the present compositions include hydrochloric acid, nitric acid, phosphoric acid, sulfuric acid, potassium hydroxide, ammonium hydroxide or ethanolamine. Appropriate acids and bases as well as appropriate amounts thereof for a particular application will be evident to one skilled in the art based upon the present disclosure.

The present invention is further directed to a method of polishing or planarizing the surface of a work piece comprising: (a) applying an aqueous slurry of the present abrasive composition to a surface of a work piece to be polished or planarized; and (b) polishing or planarizing the surface of a work piece by mechanically and chemically causing the aqueous slurry to abrade the surface of the work piece to a predetermined extent.

When used in such a method, the present composition acts to mechanically and chemically abrade and dissolve the surface of the work piece to a predetermined and desired extent. The present composition acts only at the level surface of the work piece to provide a planar, smooth, defect-free surface without adversely affecting the underlying morphology and structure of the work piece.

When used to polish or planarize the surface of work pieces, the present compositions are generally used as aqueous compositions having a solids concentration of about 5 to about 20% by weight of the present abrasive

composition as a final solids concentration. Preferably, the compositions have a final solids concentration of about 10 to about 16% by weight.

Although it has unlimited use in polishing various work pieces, the present method is advantageously used in polishing or planarizing the surfaces of interconnected, integrated circuits in semiconductor preparation. The present compositions are used to polish the dielectric layer down to a predetermined, planar level which may be composed of components of varying size, shape and hardness, as well as trenches, holes and valleys. Once the polishing of the dielectric layer such as amorphous silica is completed, a conductive layer such as tungsten may be deposited on top of the integrated surface, such as by chemical vapor deposition. This surface may then be further planarized or polished to the desired extent.

Thus, the present compositions can be used to polish or planarize the complex, anisotropic composite surfaces of semiconductor wafers to provide the extremely flat and level surfaces necessary in semiconductor technology. The present compositions can be used to polish surfaces of semiconductor wafers having a predetermined planar level, above which no portion of work piece is desired and below which exists electronic components which are defect-free. The surface can be planarized to the planar level without substantially causing adverse defects in the wafer below this planar level. Thus, the present method can be used to polish or planarize semiconductor wafers having regions of relatively less and relatively more electronic device integration density, wherein the surface of the work piece comprises a plurality of steps and a plurality of gaps between the steps.

In general, in practicing the method of the present invention, the present composition is applied to an appropriate polishing pad. The pad is then placed sufficiently proximate to the surface of the work piece at a sufficient pressure and for a sufficient time to polish or planarize the surface of the work piece by mechanically abrading the surface to a predetermined extent. Suitable polishing pads include Rodel-IC polishing pads and SUBA IV polishing pads, both available from Rodel, Inc., the assignee of this invention. The present compositions may be used in any conventional polishing or planarizing apparatus, such as the R. H. Strasbaugh 6DS-SP Planarizer manufactured by R. Howard Strasbaugh, Inc. of San Luis Obispo, Calif. or the Westech Model 372 Automatic Wafer Polisher by Westech Systems, Inc. of Phoenix, Ariz.

The present invention will now be illustrated by reference to the following specific, non-limiting examples.

EXAMPLES

Example 1

Seven sample compositions were prepared comprising the varying amounts of abrasive components set forth in Table I below. The cerium oxide used in all samples was "OPALINE" cerium oxide available from Rhonel-Poulenc Basic Chemicals Co. having a particle size of 300 to 500 nm. The fumed silica used in all samples was "AEROSIL" silica available from the Degussa Corporation having a particle size of 15 to 25 nm. The precipitated silica used in all samples was 22LS available from DeGussa having a particle size of 300 to 500 nm.

nm to about 30 nm and the precipitated silica has a particle size of about 100 nm to about 300 nm.

7. An aqueous slurry for polishing or planarizing a work piece comprising water and about 5 to about 20 weight percent of the abrasive composition of claim 1.

8. An aqueous slurry as in claim 7, wherein the cerium oxide has a particle size of about 100 nm to about 2,000 nm, the fumed silica has a particle size of about 10 nm to about 1,200 nm and the precipitated silica has a particle size of about 25 nm to about 4,000 nm.

9. An aqueous slurry as in claim 8, further comprising about 0.01 to about 2.0 percent of a surfactant.

10. An aqueous slurry as in claim 9, wherein the surfactant is selected from the group consisting of non-ionic surfactants, anionic surfactants, cationic surfactants, amphoteric surfactants and mixtures thereof.

11. An aqueous slurry as in claim 10, wherein the surfactant is selected from the group consisting of octylphenylethyleneoxide, nonylphenylethyleneoxide, octylphenoxypolyethoxyethanol, polyoxyethylene (10) octylphenol ether, nonyl phenol polyether, polyoxyethylene (20) sorbitan monooleate, poly(oxy-1,2-ethanediyl)-alpha(nonylphenyl)omega-hydroxy, aliphatic ethoxylates, salts of carboxylic acid polyamine amides, alkylammonium salts of polymers having anionic or ionic character, polycarboxylic acids, acrylic acid copolymers and mixtures thereof.

12. An aqueous slurry as in claim 11, wherein the surfactant is octylphenoxypolyethoxyethanol.

13. An aqueous slurry as in claim 8, further comprising an acidic or basic material to maintain the pH of the composition at about 4 to about 12.

14. An aqueous slurry as in claim 13, wherein the acidic or basic material maintains the pH at about 6 to about 11.4.

15. An aqueous slurry as in claim 13, wherein the acidic material is selected from the group consisting of hydrochloric acid, nitric acid, phosphoric acid and sulfuric acid, and the basic material is selected from the group consisting of potassium hydroxide, ammonium hydroxide and ethanolamine.

16. An aqueous slurry for polishing or planarizing a work piece comprising water and about 10 to about 16 percent of the abrasive composition of claim 2.

17. An aqueous slurry as in claim 16 wherein the cerium oxide has a particle size of about 100 nm to about 500 nm, the fumed silica has a particle size of about 7 nm to about 40 nm and the precipitated silica has a particle size of about 50 nm to about 2,000 nm.

18. An aqueous slurry for polishing or planarizing a work piece comprising water and about 10 to about 16% by weight of the abrasive composition of claim 3.

19. An aqueous slurry as in claim 18 wherein the cerium oxide has a particle size of about 100 nm to about 300 nm, the fumed silica has a particle size of about 10 nm to about 30 nm and the precipitated silica has a particle size of about 100 nm to about 300 nm.

20. An aqueous slurry as in claim 19 further comprising about 0.01 to about 2.0 percent of a surfactant selected from the group consisting of octylphenylethyleneoxide, nonylphenylethyleneoxide, octylphenoxypolyethoxyethanol and mixtures thereof.

21. A method of polishing or planarizing the surface of a work piece comprising:

(a) applying the aqueous slurry of any one of claims 7 through 20 to a surface of the work piece to be polished or planarized; and

(b) polishing or planarizing the surface of the work piece by mechanically and chemically causing the aqueous slurry to abrade the surface of the work piece to an extent.

22. A method as in claim 21 comprising applying the aqueous composition to a pad and then causing the pad to be sufficiently proximate the surface of the work piece at a pressure and for a time sufficient to polish or planarize the work piece.

23. A method as in claim 22 wherein the work piece is a semiconductor wafer having regions of relatively less and more electronic device integration density, the surface of the wafer having a plurality of steps and a plurality of gaps between at least some of the steps.

24. A method as in claim 23 wherein the surface of the wafer has a planar level above which no work piece material is desired and below which there exists electronic components which are desirably defect-free, the method further comprising planarizing the surface of the wafer to the planar level without substantially adverse defects in the wafer below the planar level.

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US005575885A

United States Patent [19]

Hirabayashi et al.

[11] **Patent Number:** 5,575,885[45] **Date of Patent:** Nov. 19, 1996

[54] **COPPER-BASED METAL POLISHING SOLUTION AND METHOD FOR MANUFACTURING SEMICONDUCTOR DEVICE**

[75] **Inventors:** Hideaki Hirabayashi, Tokyo;
Masatoshi Higuchi, Kawasaki, both of Japan

[73] **Assignee:** Kabushiki Kaisha Toshiba, Kawasaki, Japan

[21] **Appl. No.:** 352,611

[22] **Filed:** Dec. 9, 1994

[30] **Foreign Application Priority Data**

Dec. 14, 1993 [JP] Japan 5-313406

[51] **Int. Cl.⁶** H01L 21/00; C23F 1/00;
B44C 1/22

[52] **U.S. CL** 156/626.1; 156/636.1;
156/656.1; 156/637.1; 252/79.4; 437/228;
216/38

[58] **Field of Search** 156/626.1, 636.1,
156/656.1, 637.1; 252/79.2, 79.4; 437/225,
228 PL; 216/84, 105, 38

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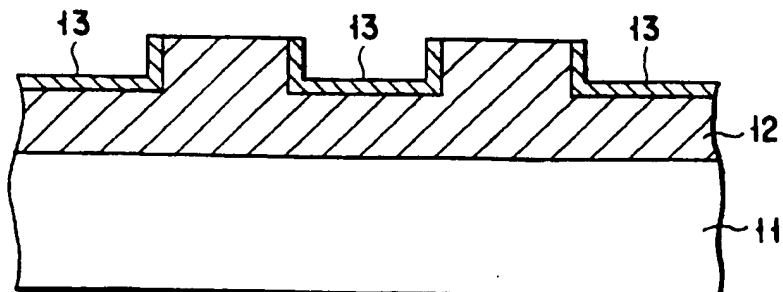
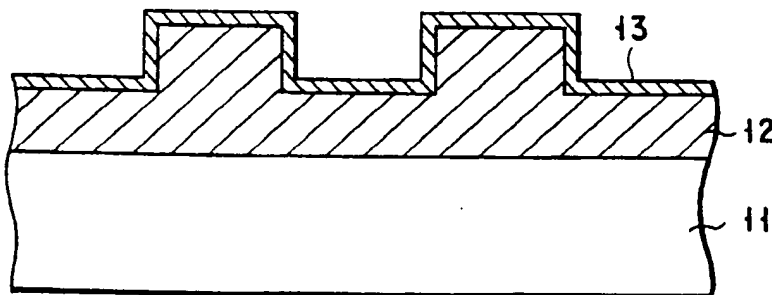
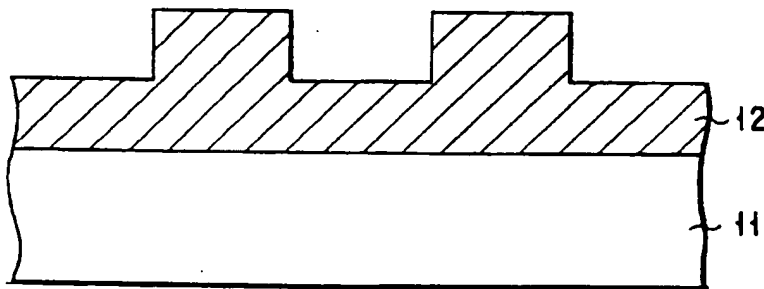
Primary Examiner—William Powell

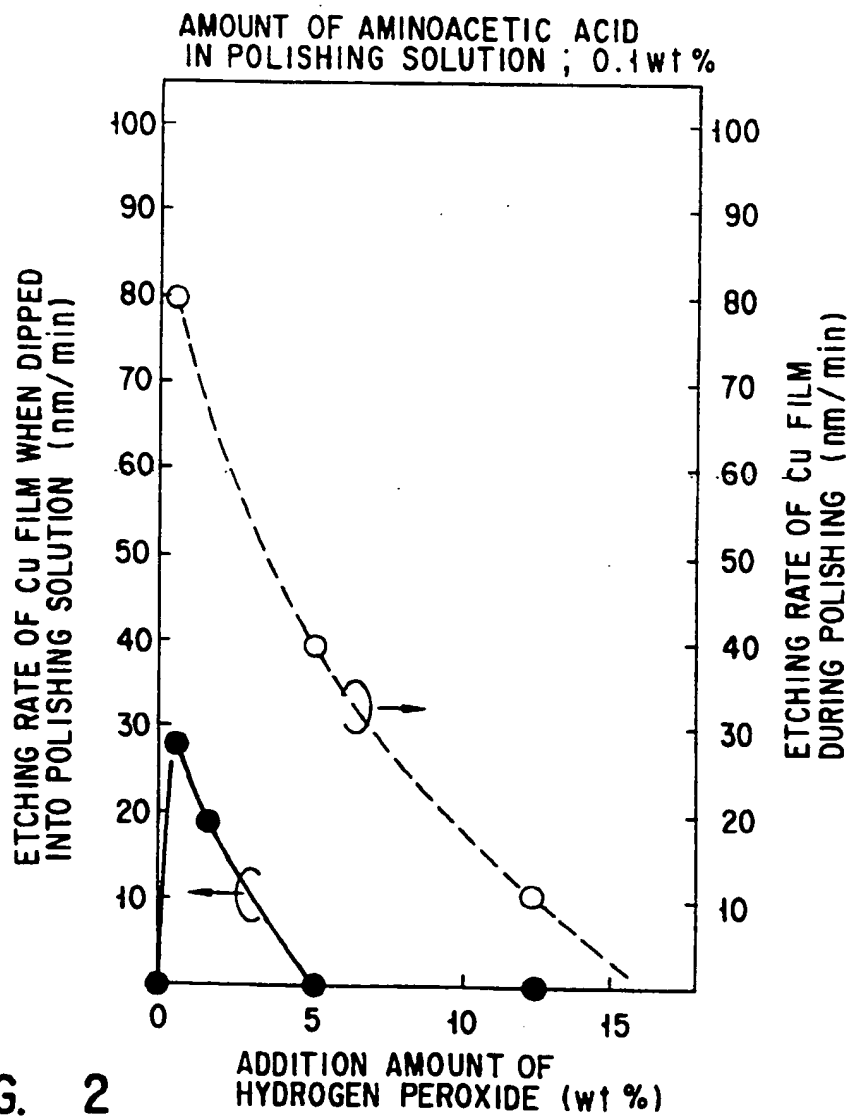
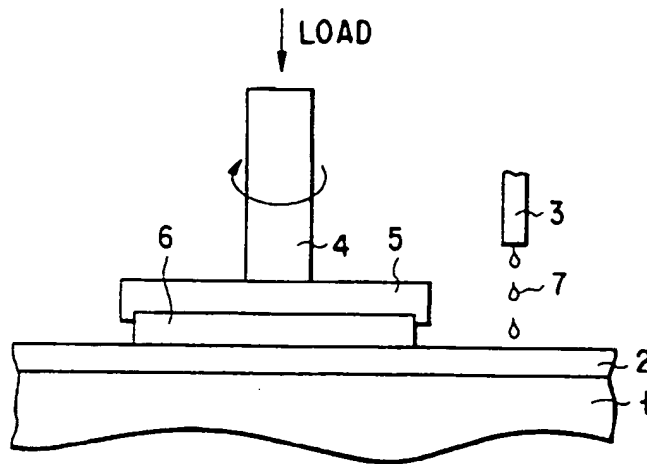
Attorney, Agent, or Firm—Oblon, Spivak, McClelland, Maier & Neustadt, P.C.

[57] **ABSTRACT**

Disclosed is a copper-based metal polishing solution which hardly dissolves a Cu film or a Cu alloy film when the film is dipped into the solution, and has a dissolution velocity during polishing several times higher than that during dipping. This copper-based metal polishing solution contains at least one organic acid selected from aminoacetic acid and amidosulfuric acid, an oxidizer, and water.

66 Claims, 14 Drawing Sheets





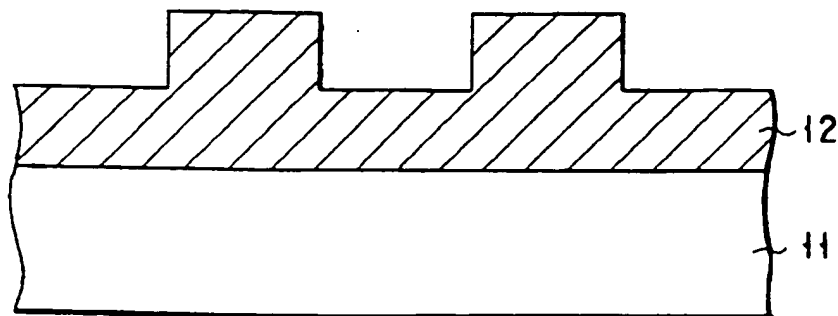


FIG. 3A

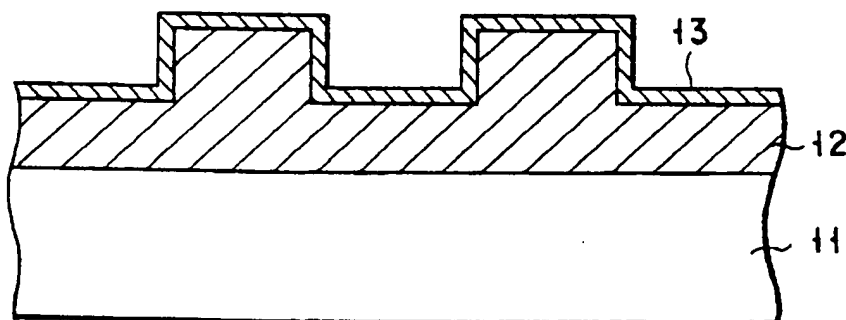


FIG. 3B

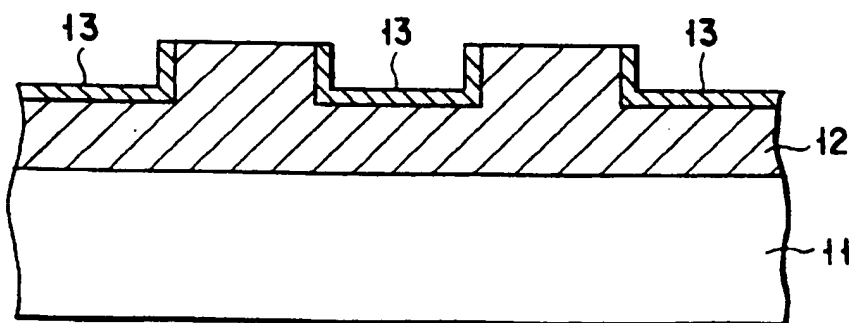


FIG. 3C

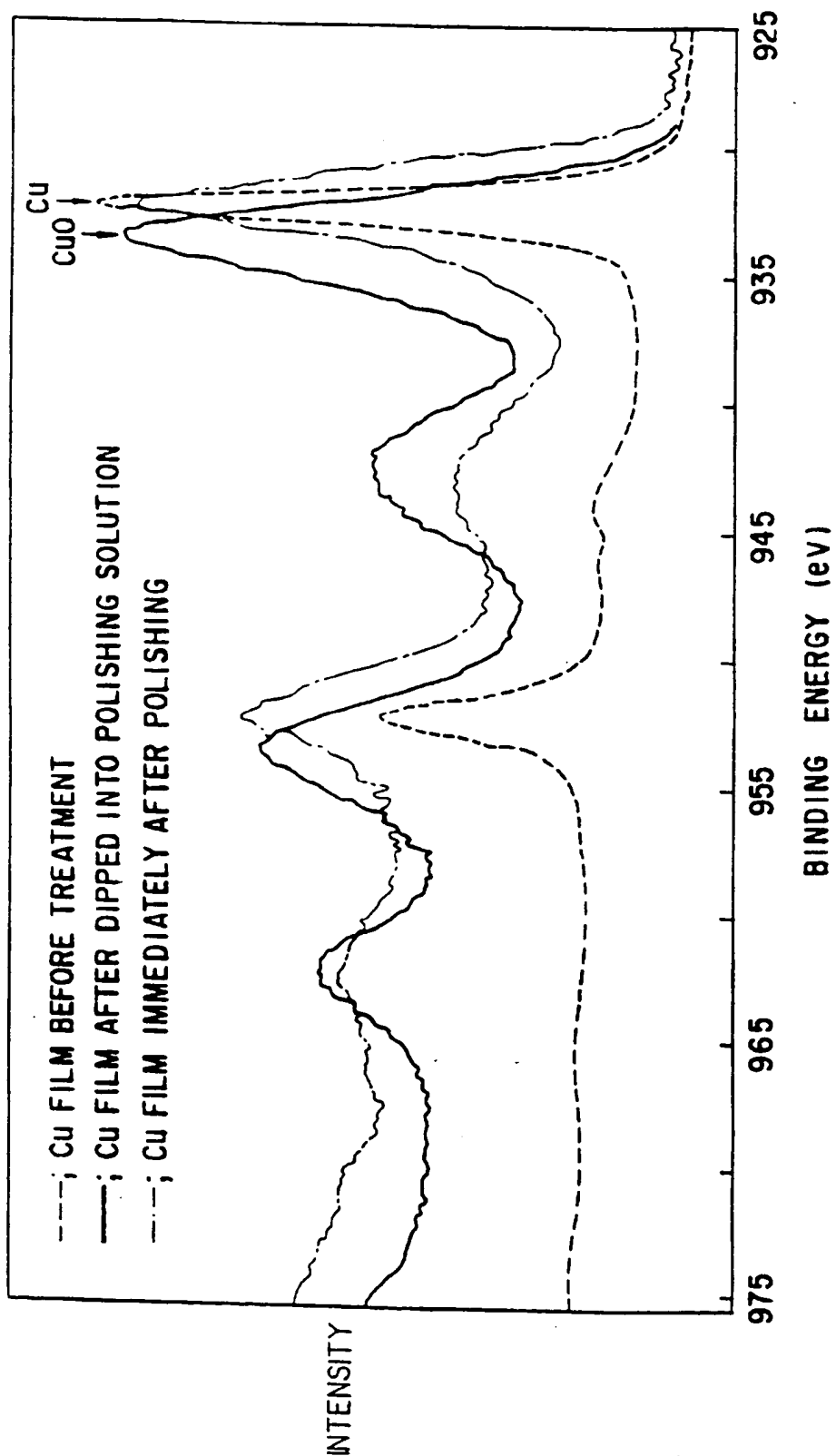


FIG. 4

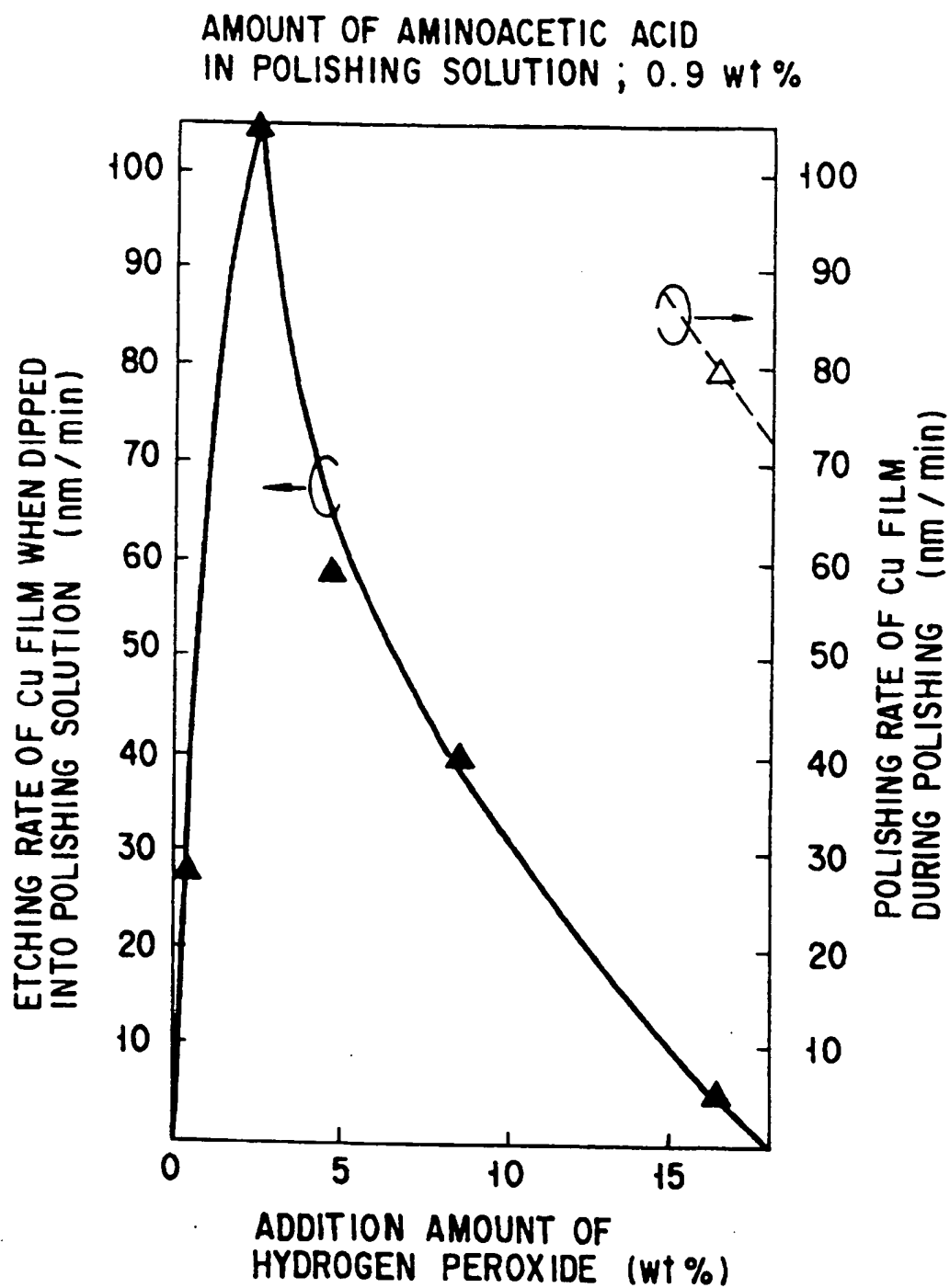


FIG. 5

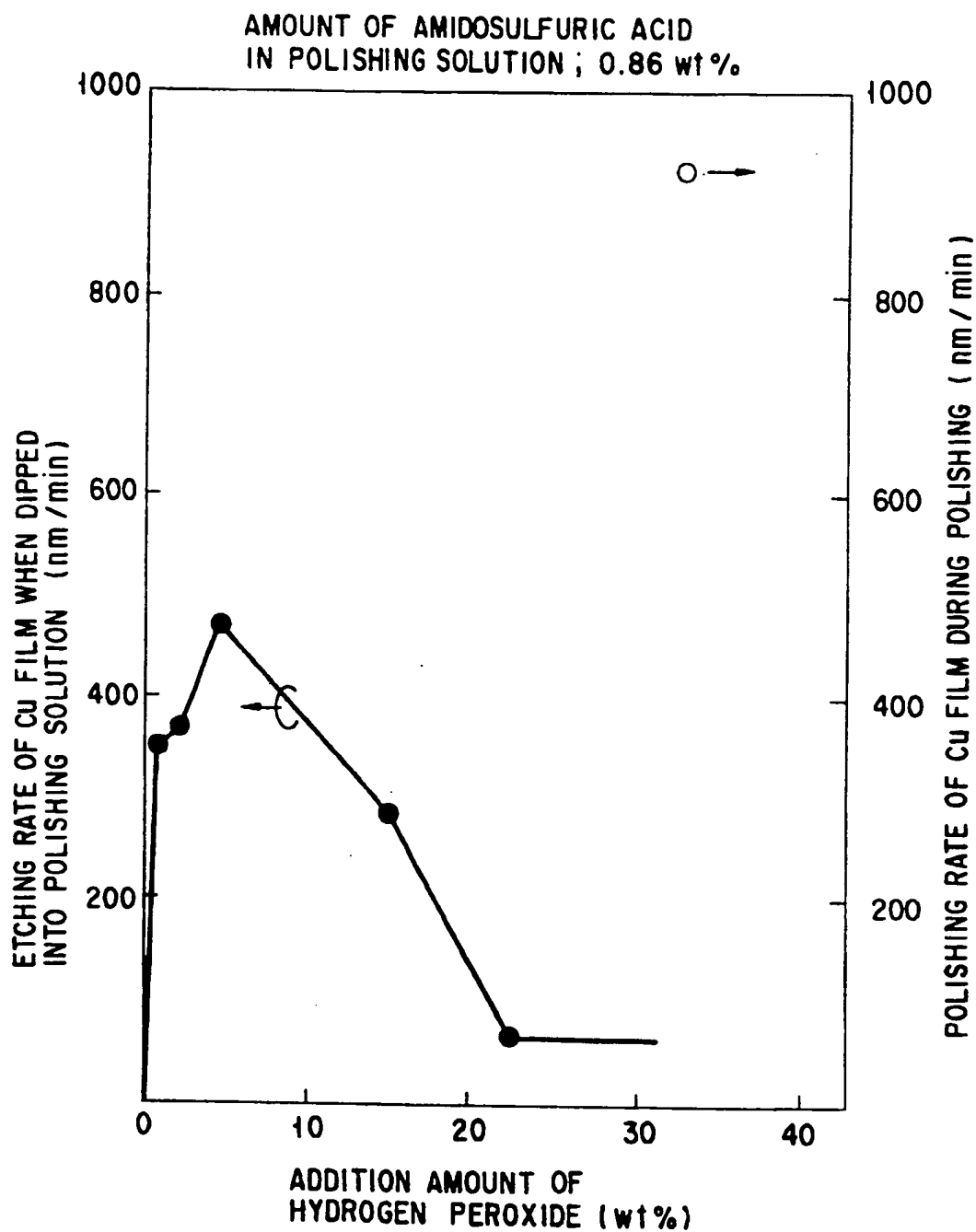


FIG. 6

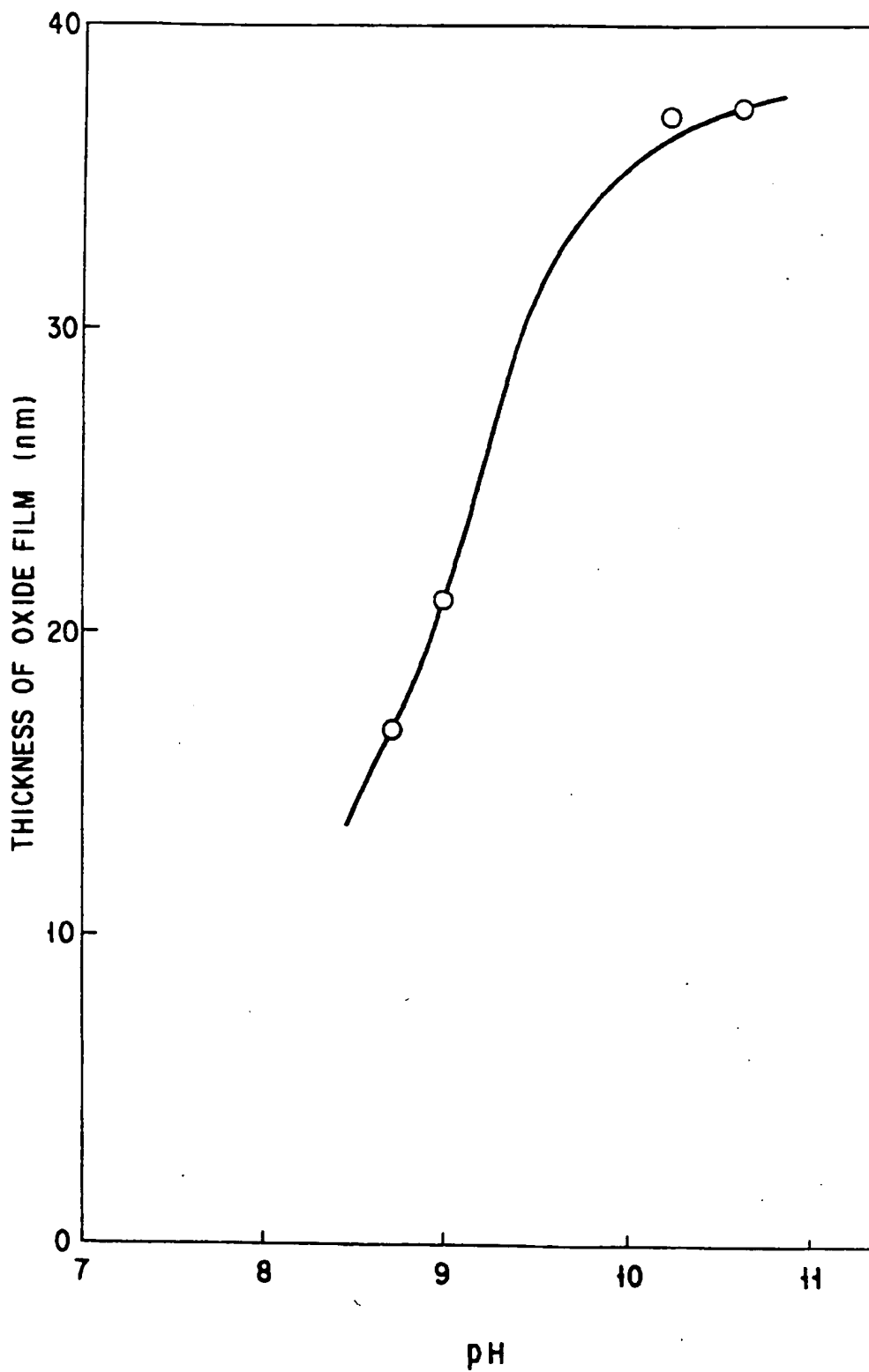


FIG. 7

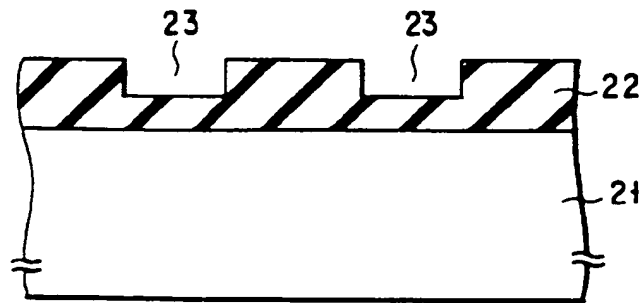


FIG. 8A

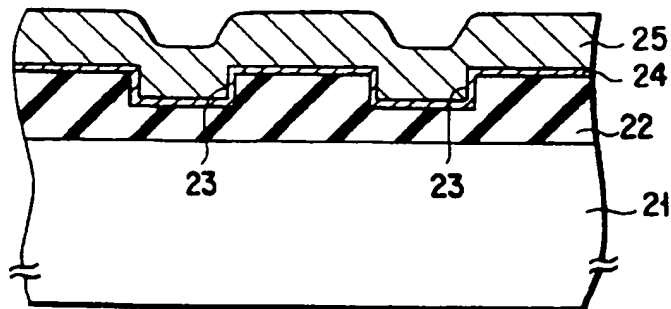


FIG. 8B

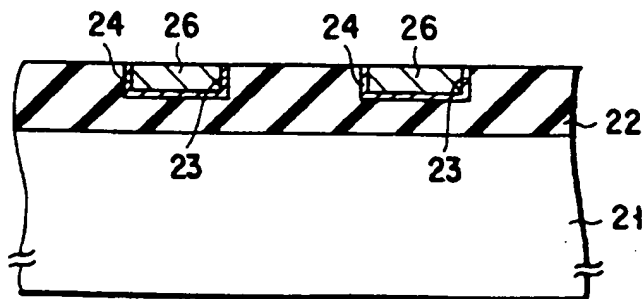


FIG. 8C

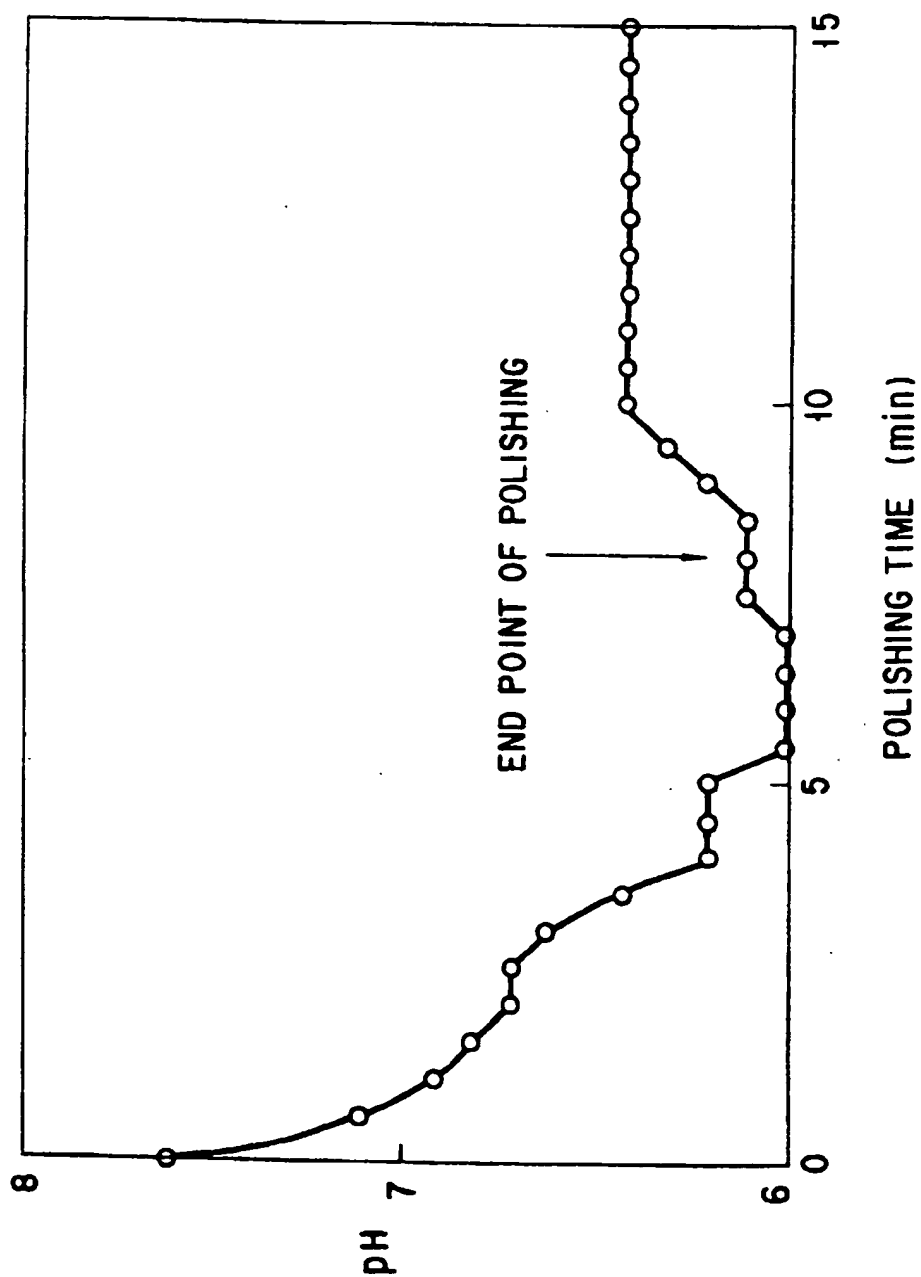


FIG. 9

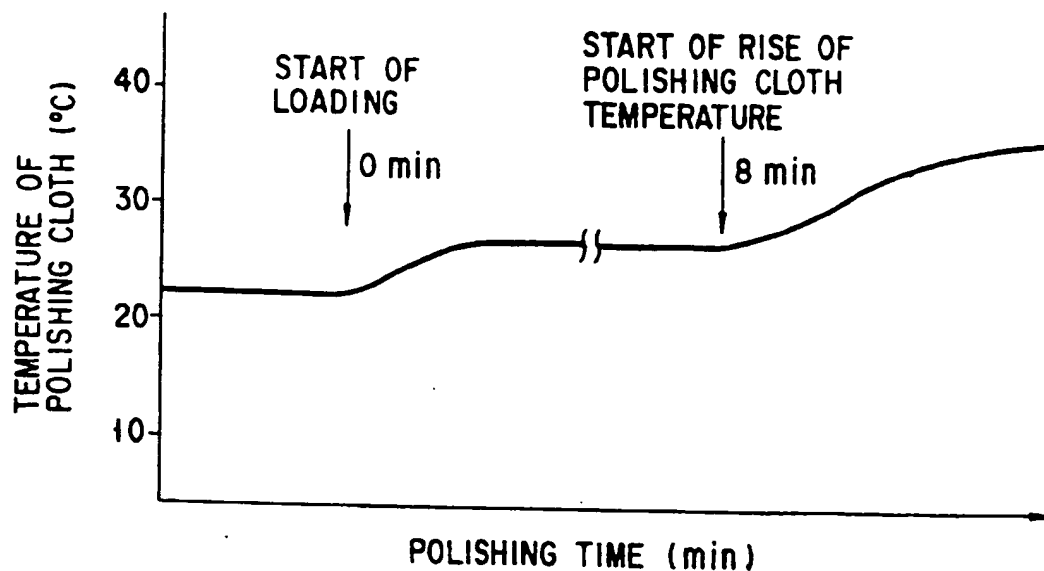


FIG. 10

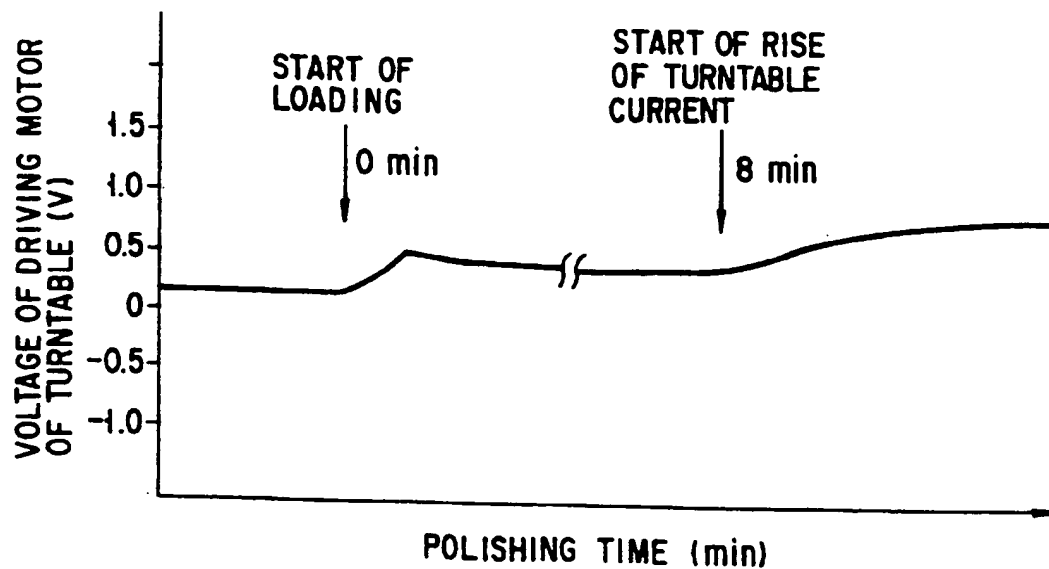


FIG. 11

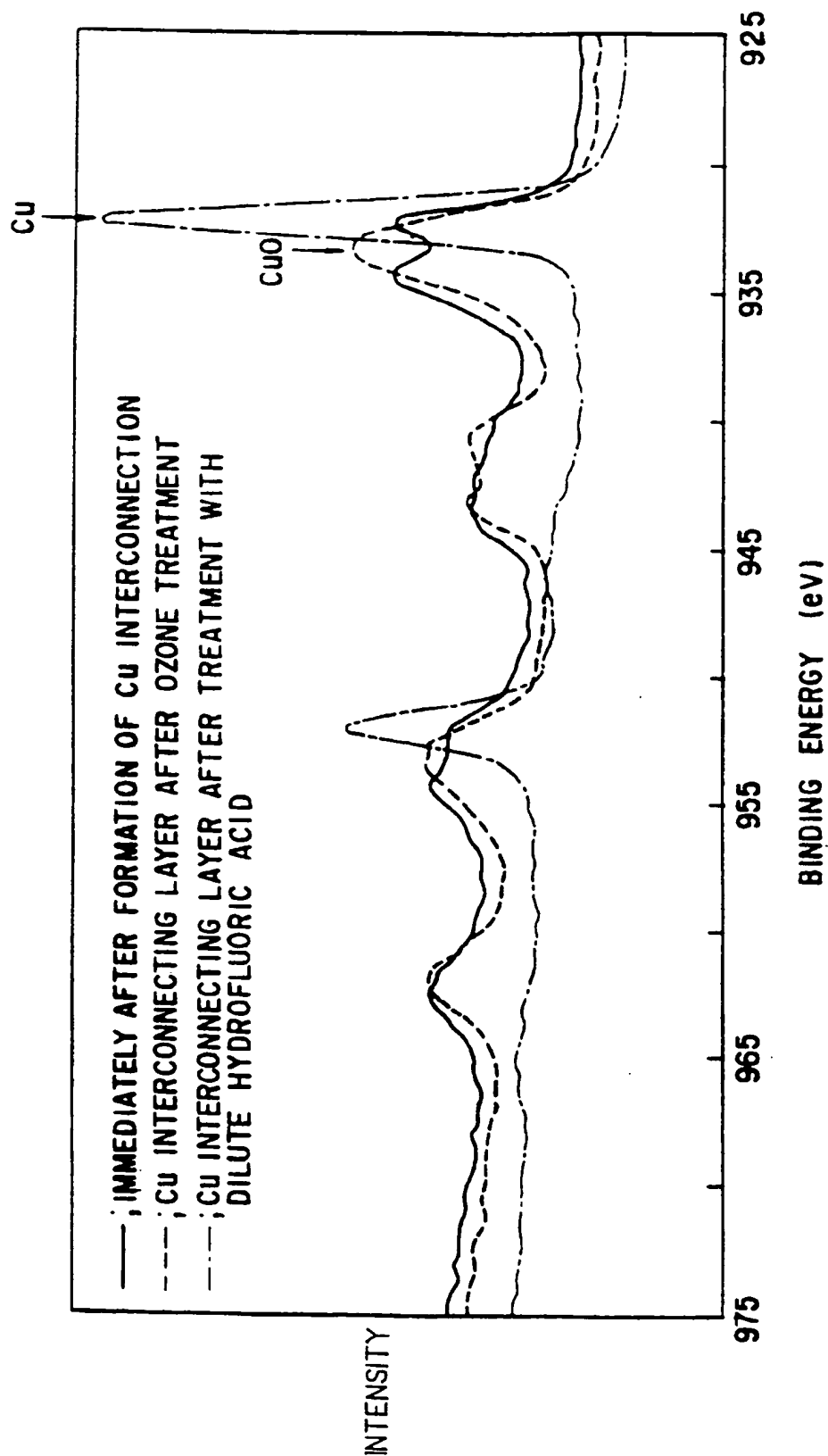


FIG. 12

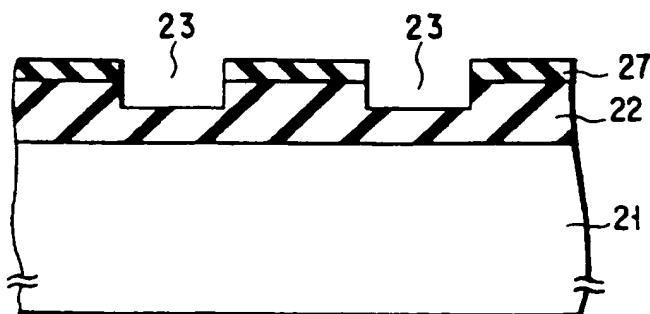


FIG. 13A

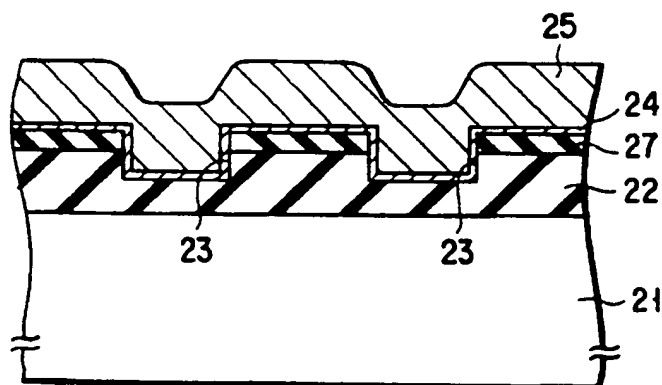


FIG. 13B

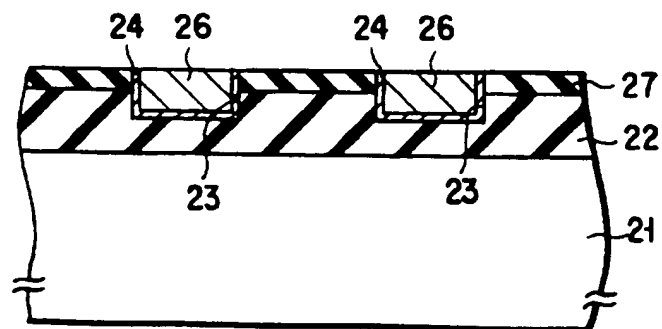


FIG. 13C

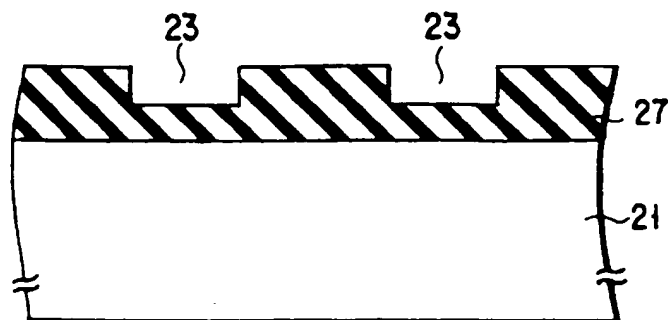


FIG. 14A

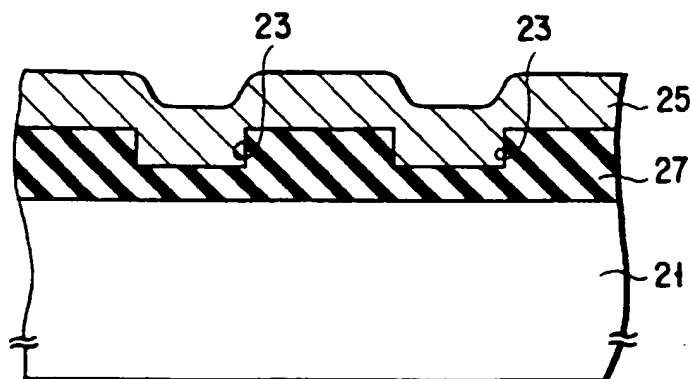


FIG. 14B

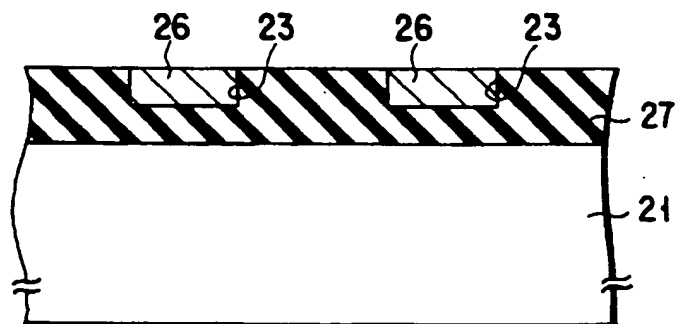


FIG. 14C

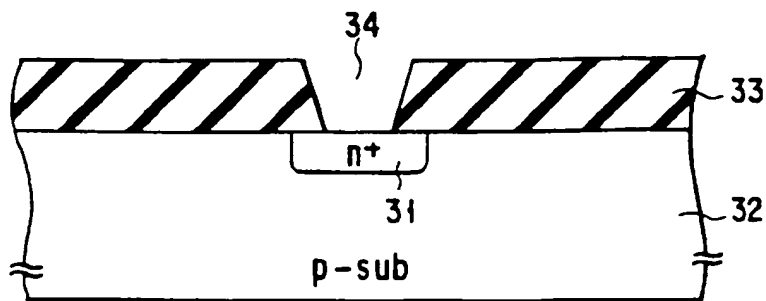


FIG. 15A

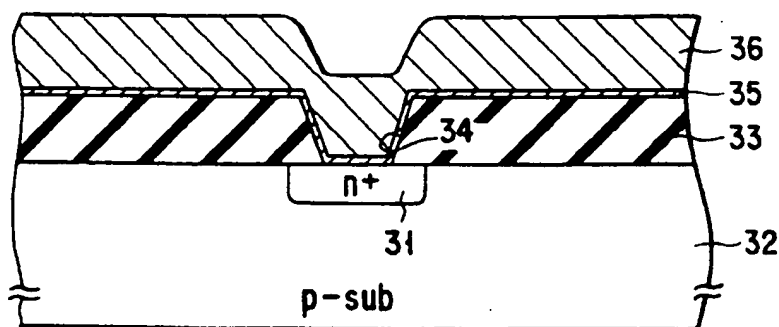


FIG. 15B

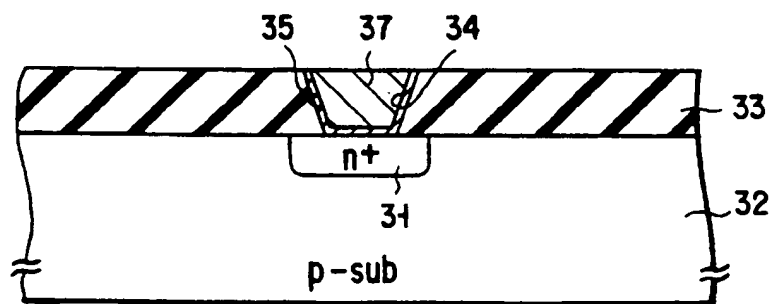


FIG. 15C

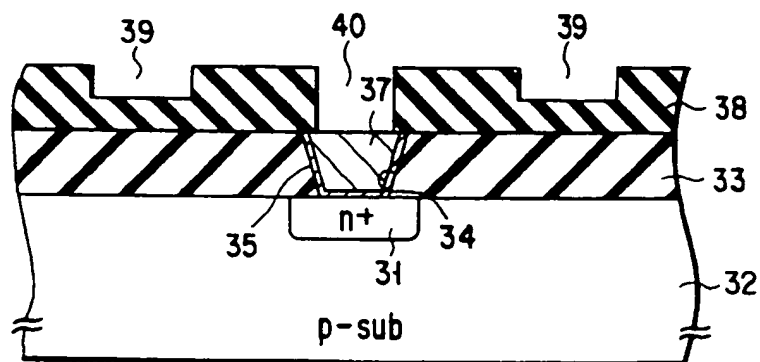


FIG. 15D

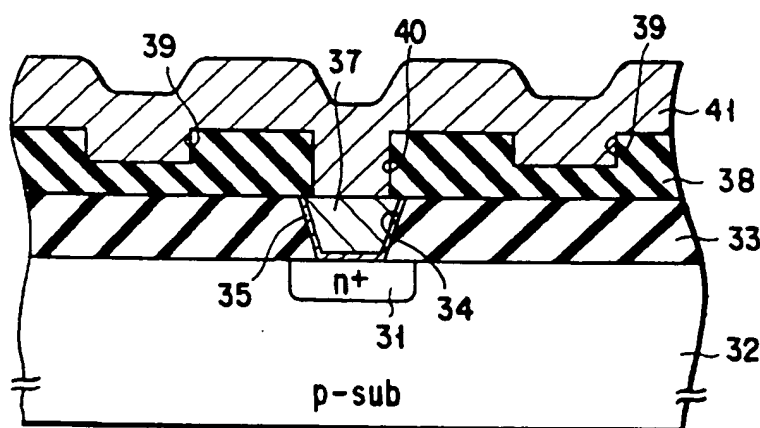


FIG. 15E

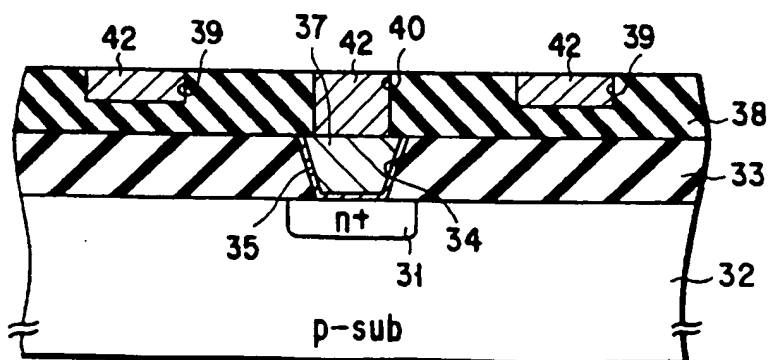


FIG. 15F

COPPER-BASED METAL POLISHING SOLUTION AND METHOD FOR MANUFACTURING SEMICONDUCTOR DEVICE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a copper-based metal polishing solution and a method for manufacturing a semiconductor device.

2. Description of the Related Art

A polishing solution for a Cu film or a Cu-alloy film, which consists of a slurry of amine-based colloidal silica or a slurry added with $K_3Fe(CN)_6$, $K_4(CN)_6$, or $Co(NO_3)_2$, is disclosed in J. Electrochem. Soc., Vol. 138, No. 11, 3460 (1991), VMIC Conference, ISMIC-101/92/0156 (1992) or VMIC Conference, ISMIC-102/93/0205 (1993).

Unfortunately, the above polishing solution has the following problem since there is no difference between the Cu film dissolution velocity of the polishing solution during dipping and that during polishing.

In the formation of an interconnecting layer as one manufacturing step of semiconductor devices, an etch-back technique is employed in order to remove steps from the device surface. This etch-back technique is a method in which a trench is formed in an insulating film on a semiconductor substrate, and a Cu film is deposited on the insulating film including the trench and polished by using a polishing solution, thereby forming a buried interconnecting layer by leaving the Cu film behind only in the trench. After this etch-back step, the Cu interconnecting layer remaining in the trench is brought into contact with a polishing solution. Therefore, if a polishing solution of the composition discussed above by which no difference is obtained between the Cu film etching rate during dipping and that during polishing, the Cu interconnecting layer is further etched by the polishing solution. As a result, the surface of the Cu interconnecting layer becomes lower than the surface of the insulating film. This makes it difficult to form an interconnecting layer whose surface is level with the surface of the insulating film, resulting in a low flatness. In addition, the resistance of a buried Cu interconnecting layer formed in this manner becomes higher than that of a Cu interconnecting layer which is so buried that its surface is level with the surface of an insulating film.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a copper-based metal polishing solution which hardly etches copper (Cu) or a copper alloy (Cu alloy) when this Cu or Cu alloy is dipped into the solution, and dissolves the Cu or Cu alloy during polishing with an etching rate several times to several ten times higher than that during the dipping.

It is another object of the present invention to provide a method for manufacturing a semiconductor device, in which a trench and/or an opening is formed in an insulating film on a semiconductor substrate, and an interconnection material film deposited on the insulating film and consisting of copper (Cu) or a copper alloy (Cu alloy) can be etched back within a short time period and at the same time a buried interconnecting layer whose surface is level with the surface of the insulating film can be formed.

It is still another object of the present invention to provide a method for manufacturing a semiconductor device, in which a trench and/or an opening is formed in an insulating film on a semiconductor substrate, an interconnection material film deposited on the insulating film and consisting of Cu or a Cu alloy can be etched back within a short time period to form a buried interconnecting layer whose surface is level with the surface of the insulating film, and the surface of the insulating film and the like after the etch back can be cleaned well.

According to the present invention, there is provided a copper-based metal polishing solution containing at least one organic acid selected from the group consisting of aminoacetic acid and amidosulfuric acid, an oxidizer, and water.

According to the present invention, there is also provided a method for manufacturing a semiconductor device, comprising the steps of:

forming at least one member selected from the group consisting of a trench and an opening corresponding to a shape of an interconnecting layer in an insulating film on a semiconductor substrate;

depositing an interconnection material film consisting of copper (Cu) or a copper alloy (Cu alloy) on the insulating film including at least one member selected from the group consisting of a trench and an opening; and

polishing the interconnection material film until a surface of the insulating film is exposed by using a polishing solution containing at least one organic acid selected from the group consisting of aminoacetic acid and amidosulfuric acid, an oxidizer, and water, thereby forming a buried interconnecting layer in the insulating film such that surfaces of the interconnecting layer and the insulating film are level with each other.

Furthermore, according to the present invention, there is provided a method for manufacturing a semiconductor device, comprising the steps of:

forming at least one member selected from the group consisting of a trench and an opening corresponding to a shape of an interconnecting layer in an insulating film on a semiconductor substrate;

depositing an interconnection material film consisting of copper (Cu) or a copper alloy (Cu alloy) on the insulating film including at least one member selected from the group consisting of a trench and an opening;

polishing the interconnection material film until a surface of the insulating film is exposed by using a polishing solution containing at least one organic acid selected from the group consisting of aminoacetic acid and amidosulfuric acid, an oxidizer, and water, thereby forming a buried interconnecting layer in the insulating film such that surfaces of the interconnecting layer and the insulating film are level with each other; and

treating the surface of the insulating film including the interconnecting layer with an aqueous dissolved ozone solution and then with an aqueous dilute hydrofluoric acid solution.

Additional objects and advantages of the invention will be set forth in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and obtained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate presently

preferred embodiments of the invention, and together with the general description given above and the detailed description of the preferred embodiments given below, serve to explain the principles of the invention.

FIG. 1 is a schematic view showing a polishing apparatus for use in the process of polishing of the present invention;

FIG. 2 is a graph showing the characteristics of a polishing solution composed of 0.1 wt % aminoacetic acid, hydrogen peroxide, and water, i.e., showing the relationship between the amount of hydrogen peroxide, the etching rate of a Cu film when the film was dipped into the solution, and the polishing rate of the Cu film during polishing;

FIGS. 3A to 3C are sectional views showing the states of a Cu film with projections when the film was dipped into a polishing solution composed of aminoacetic acid, hydrogen peroxide, and water, and was polished by using a polishing apparatus;

FIG. 4 is a graph showing the spectra of the surface of a Cu film obtained by XPS (X-ray Photoelectron Spectroscopy) before the treatment, after the film was dipped into the polishing solution of the present invention, and after the film was polished;

FIG. 5 is a graph showing the characteristics of a polishing solution composed of 0.9 wt % aminoacetic acid, hydrogen peroxide, and water, i.e., showing the relationship between the amount of hydrogen peroxide, the etching rate of a Cu film when the film was dipped into the solution, and the polishing rate of the Cu film during polishing;

FIG. 6 is a graph showing the characteristics of a polishing solution composed of amidosulfuric acid, hydrogen peroxide, and water, i.e., showing the relationship between the amount of hydrogen peroxide, the etching rate of a Cu film when the film was dipped into the solution, and the polishing rate of the Cu film during polishing;

FIG. 7 is a graph showing a change in the thickness of an oxide layer formed on the surface of a Cu film as a function of the pH of the polishing solution of the present invention;

FIGS. 8A to 8C are sectional views showing manufacturing steps of the semiconductor device in Example 1 of the present invention;

FIG. 9 is a graph showing a change in the pH of the polishing solution during polishing (an etch-back step) in Example 1;

FIG. 10 is a graph showing a change in the temperature of a polishing cloth during the polishing (the etch-back step) in Example 1;

FIG. 11 is a graph showing a change in the voltage of a driving motor of a turntable during the polishing (the etch-back step) in Example 1;

FIG. 12 is a graph showing the spectra of the surface of a Cu interconnecting layer obtained by XPS immediately after formation, after an ozone treatment, and after a treatment using dilute hydrofluoric acid in Example 1 of the present invention;

FIGS. 13A to 13C are sectional views showing manufacturing steps of the semiconductor device in Example 2 of the present invention;

FIGS. 14A to 14C are sectional views showing manufacturing steps of the semiconductor device in Example 3 of the present invention; and

FIGS. 15A to 15F are sectional views showing manufacturing steps of the semiconductor device in Example 4 of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A copper-based metal polishing solution according to the present invention contains at least one organic acid selected from aminoacetic acid and amidosulfuric acid, an oxidizer, and water. When Cu or a Cu alloy is dipped in this polishing solution, the polishing solution forms an oxide layer, which functions as an etching barrier, on the surface of the Cu or Cu alloy by the oxidizing action of the oxidizer. During polishing of the Cu or Cu alloy, the organic acid in the solution etches the Cu or Cu alloy which is exposed by mechanically removing the oxide layer. Therefore, etching of the Cu or Cu alloy is suppressed or prevented by the oxide layer while it is dipped into the polishing solution. During the polishing, the exposed Cu or Cu alloy is physically polished and etched by the organic acid contained in the polishing solution. This sufficiently increases the difference between the etching rate of the Cu or Cu alloy during the dipping and that during the polishing.

As the oxidizer, it is possible to use, e.g., hydrogen peroxide (H_2O_2) or soda hypochlorite ($NaClO$).

In the polishing solution, it is preferable that 0.01 to 10 wt % of the organic acid be contained and the weight ratio of the organic acid to the oxidizer be 1 to 20 or more. The content of the organic acid and the content ratio of the organic acid to the oxidizer in the polishing solution are thus defined for the reasons explained below.

If the content of the organic acid is smaller than 0.01 wt %, the polishing rate (primarily the chemical dissolution velocity) of Cu or a Cu alloy during polishing may decrease. On the other hand, if the content of the organic acid is larger than 10 wt %, etching of Cu or a Cu alloy may proceed exceedingly when the Cu or Cu alloy is dipped into the polishing solution to thereby nullify the difference between the etching rate during the dipping and that during polishing. The content of the organic acid is more preferably 0.01 to 1 wt %.

If the weight ratio of the organic acid to the oxidizer is 1 to less than 20, it may become impossible to obtain a sufficient etching rate difference between dipping of Cu or a Cu alloy and polishing of it. The content ratio of the organic acid to the oxidizer in the polishing solution is preferably 1 to 40 or more, and more preferably 1 to 100 or more.

It is desirable that the upper-limiting ratio of the oxidizer to the organic acid be defined by the content of the oxidizer. For example, the content of the oxidizer is preferably 30 wt %. If the content of the oxidizer exceeds 30 wt %, an oxide layer may immediately form on the exposed surface during polishing of Cu or a Cu alloy to result in a low polishing rate.

If the content of the organic acid is to be set at the lower-limiting value (0.01 wt %) within the range defined above, it is preferable that the content ratio of the organic acid to the oxidizer be set at 1 to 40 or more as a weight ratio.

The polishing solution according to the present invention may contain an alkaline agent for adjusting the pH of the solution between 9 and 14, in addition to the organic acid and the oxidizer. Suitable examples of this alkaline agent are potassium hydroxide and quinoline.

The polishing solution according to the present invention may contain abrasive grains, such as silica grains, alumina grains, cerium oxide grains, or zirconia grains, in addition to the organic acid and the oxidizer. These abrasive grains can be used in the form of a mixture of two or more types of grains.

The abrasive grains preferably have a mean grain size of 0.02 to 0.1 μm .

The abrasive grains are preferably added in an amount of 1 to 14 wt %. If the addition amount of the abrasive grains is less than 1 wt %, the effect of the grains becomes difficult to achieve. If, on the other hand, the addition amount of the abrasive grains is more than 14 wt %, the viscosity of the polishing solution is increased to make the solution difficult to handle. The addition amount of the abrasive grains is more preferably 3 to 10 wt %.

A polishing apparatus shown in FIG. 1 is used to polish a Cu film or a Cu alloy film formed on, e.g., a substrate by using the copper-based metal polishing solution according to the present invention. That is, a polishing pad 2 made of, e.g., cloth is covered on a turntable 1. A supply pipe 3 for supplying a polishing solution is arranged above the polishing pad 2. A substrate holder 5 having a support shaft 4 on its upper surface is arranged above the polishing pad 2 so as to be vertically movable and rotatable. In the polishing apparatus with this arrangement, the holder 5 holds a substrate 6 such that the surface (e.g., a Cu film) to be polished faces the pad 2. While a polishing solution 7 of the composition discussed above is supplied from the supply pipe 3, and a desired load is applied from the support shaft 4 to the substrate 6 toward the polishing pad 2. The Cu film on the substrate is polished while the turntable 1 and the holder 5 are rotated in the opposite direction.

The copper-based metal polishing solution according to the present invention as described above contains at least one organic acid selected from aminoacetic acid and amidosulfuric acid, an oxidizer, and water. Therefore, this polishing solution hardly etches Cu or Cu alloy when Cu or a Cu alloy is dipped into the solution (the etching rate is preferably 100 nm/min or less), and has an etching rate during polishing several times to several ten times higher than that during the dipping.

More specifically, an organic acid (e.g., aminoacetic acid) as one component of the polishing solution has a property of producing a complex by reacting with a hydrate of Cu, as indicated by the following reaction formula.



Cu does not react with a solution mixture of aminoacetic acid and water. In this reaction system, the addition of an oxidizer (e.g., hydrogen peroxide) allows the reaction to proceed in the direction indicated by the arrow in the above formula, thereby etching Cu.

FIG. 2 shows plots of the etching rate of a Cu film formed on a substrate during dipping and the etching rate of the film during polishing in a polishing solution composed of aminoacetic acid, hydrogen peroxide, and water, when the content of aminoacetic acid was kept constant at 0.1 wt % and the content of hydrogen peroxide was varied. Note that the polishing was done by using the polishing apparatus illustrated in FIG. 1. That is, a substrate on which a Cu film was formed was held upside down by the substrate holder 5 so that the Cu film faced the polishing pad 2 consisting of SUBA800 (tradename) manufactured by Rodcl Nitta Corp. A load of 400 g/cm² was applied from the support shaft 4 to the substrate toward the polishing pad 2. While the turntable 1 and the holder 5 were rotated in the opposite directions at a rotating speed of 100 rpm, the polishing solution was supplied from the supply pipe 3 to the polishing pad 2 at a rate of 12.5 ml/min to perform polishing.

As is apparent from FIG. 2, the Cu film was not etched at all when dipped into a polishing solution added with no hydrogen peroxide. When the polishing solution contained a small amount of hydrogen peroxide, however, the Cu film

was briskly etched. This is so because a hydrate of Cu was produced by hydrogen peroxide contained in the polishing solution and aminoacetic acid reacted with this Cu hydrate to produce a complex, thereby etching Cu. It is also evident from FIG. 2 that the Cu film etching rate was lowered as the content of hydrogen peroxide was increased further, and became zero when the content of hydrogen peroxide reached 5 wt %. The reason for this is assumed that an oxide layer which prevents etching by the polishing solution is formed on the surface of a Cu film if the content of hydrogen peroxide is increased.

In effect, a Cu film 12 having projections was formed on a substrate 11, as shown in FIG. 3A, and the resultant substrate 11 was dipped into a polishing solution (containing 0.1 wt % of aminoacetic acid and 13 wt % of hydrogen peroxide) of the composition, FIG. 2, by which the etching rate was lowered. Consequently, as depicted in FIG. 3B, an oxide layer 13 was formed on the surface of the Cu film 12. In addition, the surface of the Cu film was analyzed with XPS after the substrate was dipped into the polishing solution. The result was that a spectrum indicated by the solid line in FIG. 4 appeared. This also demonstrates the formation of an oxide layer. Note that the dotted line in FIG. 4 represents the spectrum immediately after the Cu film was formed on the substrate and before the treatment.

It was found that the polishing rate of a Cu film when polishing was done by using the polishing apparatus in FIG. 1 and the polishing solution containing 0.1 wt % of aminoacetic acid and 13 wt % of hydrogen peroxide was approximately 10 nm/min, which was sufficiently higher than the Cu film etching rate during the dipping, as shown in FIG. 2. This rise in the Cu film polishing rate resulting from the polishing was due to the reason explained below. That is, when the Cu film 12 on the surface of which the oxide layer 13 was formed, FIG. 3B, was polished with a polishing pad soaked with the above polishing solution, the oxide layer 13 on each projecting portion of the Cu film 12 was mechanically polished by the pad to expose pure Cu to the surface as illustrated in FIG. 3C. As a consequence, active chemical polishing was brought about by the action of aminoacetic acid and hydrogen peroxide contained in the polishing solution. That is, in the polishing step pure Cu is constantly exposed to the surface to be polished of a Cu film, and this permits chemical etching by aminoacetic acid and hydrogen peroxide contained in the polishing solution. In effect, when the surface of a Cu film immediately after polishing was analyzed by XPS, a spectrum indicated by the alternate long and short dashed line in FIG. 4 appeared, demonstrating the exposure of Cu.

FIG. 5 shows plots of the etching rate of a Cu film formed on a substrate during dipping and the polishing rate of the film during polishing in a polishing solution composed of aminoacetic acid, hydrogen peroxide, and water, when the content of aminoacetic acid was held constant at 0.9 wt % and the content of hydrogen peroxide was varied. Note that the polishing was done following the same procedures as discussed above by using the polishing apparatus shown in FIG. 1. As can be seen from FIG. 5, the Cu film was not etched at all when dipped into a polishing solution added with no hydrogen peroxide. However, the Cu film was vigorously etched when a small amount of hydrogen peroxide was added to the polishing solution. FIG. 5 also reveals that the Cu film etching rate decreased as the content of hydrogen peroxide was increased further, and became zero when the content of hydrogen peroxide reached about 18 wt %. The reason for this is considered that an oxide layer which prevents etching by the polishing solution is formed

on the surface of a Cu film if the content of hydrogen peroxide is increased. A Cu film was polished following the same procedures as described above by using a polishing solution containing 15 wt % of hydrogen peroxide. As a result, the Cu film was polished at a rate of approximately 85 nm/min, i.e., the etching rate during the polishing was sufficiently higher than that during the dipping. However, the polishing rate of a Cu film during polishing was about 60 nm/min even by the use of a polishing solution which contained 20 wt % of hydrogen peroxide and by which etching of a Cu film was reliably prevented during dipping, i.e., a polishing solution in which the content ratio of aminoacetic acid to hydrogen peroxide was 1 to about 20 as a weight ratio. Therefore, the etching rate during the polishing was sufficiently higher than that during the dipping.

FIG. 6 shows plots of the etching rate of a Cu film formed on a substrate during dipping and the polishing rate of the film during polishing in a polishing solution composed of amidosulfuric acid as an organic acid, hydrogen peroxide, and water, when the content of amidosulfuric acid was held constant at 0.86 wt % and the content of hydrogen peroxide was varied. Note that the polishing was done following the same procedures as discussed above by using the polishing apparatus depicted in FIG. 1. It is evident from FIG. 6 that the Cu film was not etched at all when a polishing solution added with no hydrogen peroxide was used, but was actively etched when the polishing solution contained a small amount of hydrogen peroxide. It is also apparent from FIG. 6 that the Cu film etching rate was lowered as the content of hydrogen peroxide was increased, and was 50 nm/min when the content of hydrogen peroxide was about 22 wt % or more. The reason for this is assumed that an oxide layer which prevents etching by the polishing solution is formed on the surface of a Cu film if the content of hydrogen peroxide is increased. A Cu film was polished following the same procedures as described above by using a polishing solution which contained 30 wt % of hydrogen peroxide, i.e., in which the content ratio of amidosulfuric acid to hydrogen peroxide was 1 to about 35 as a weight ratio. Consequently, the Cu film was polished at a rate of approximately 950 nm/min. That is, the etching rate during the polishing was sufficiently high, about 19 times higher than that during the dipping.

As discussed above, the polishing solution according to the present invention hardly etches Cu or Cu alloy when Cu or a Cu alloy is dipped into the solution, and has an etching rate during polishing several times to several ten times higher than that during dipping. For this reason, it is possible to avoid the problem that, for example, the Cu etching amount varies depending on the supply timing of a polishing solution in the polishing step. This allows an easy polishing operation. In addition, an oxide layer is formed on a Cu film on a substrate by hydrogen peroxide, as mentioned earlier, when the Cu film comes into contact with the polishing solution after being polished by the polishing apparatus. This prevents so-called over-etching in which the Cu film continues to be etched after the polishing. Furthermore, as illustrated in FIG. 3C, in the polishing step the Cu film having projections is sequentially etched from the surface of each projection in contact with the polishing pad while the side surfaces of the film remain unetched. Therefore, the polishing solution is very suitable for an etch-back technique (to be described later).

By adjusting the pH of the polishing solution according to the present invention between 9 and 14 by adding an alkaline agent such as potassium hydroxide to the solution, an oxide layer having a good etching barrier property with respect to

the polishing solution can be formed on the surface of Cu or a Cu alloy when the Cu or Cu alloy is dipped into the solution. It is also possible to control the thickness of the oxide layer formed on the surface of Cu or a Cu alloy. FIG. 7 is a graph showing a change in the thickness of an oxide layer formed on the surface of a Cu film formed on a substrate when the Cu film was dipped into a polishing solution which contained 0.9 wt % of aminoacetic acid and 12 wt % of hydrogen peroxide and in which the pH was adjusted between 8.5 and 11 by addition of potassium hydroxide. As shown in FIG. 7, the thickness of the oxide layer formed on the surface of the Cu film increases as the pH rises.

The polishing solution whose pH is adjusted between 9 and 14 allows formation of an oxide layer having a good etching barrier property on the surface of Cu or a Cu alloy when the Cu or Cu alloy is dipped into the polishing solution. Therefore, even if the content of an organic acid such as aminoacetic acid in the polishing solution is increased, Cu is hardly etched when Cu or a Cu alloy is dipped into the solution. During polishing, on the other hand, this increase in the content of the organic acid makes it possible to increase the etching rate of the Cu or Cu alloy. Consequently, the difference between the etching rate during the dipping and that during the polishing can be increased as compared with a polishing solution added with no alkaline agent. The result is a reduced polishing time of the Cu or Cu alloy.

By adding abrasive grains such as silica grains to the polishing solution according to the present invention, it is possible to improve the polishing rate during polishing of Cu or a Cu alloy compared to a polishing solution not added with the abrasive grains. As examples, polishing solutions were prepared by adding about 9 wt % of silica grains with a mean grain size of 30 nm, alumina grains with a mean grain size of 740 nm, cerium oxide grains with a mean grain size of 1300 nm, and zirconia grains with a mean grain size of 1100 nm to an aqueous solution containing 0.1 wt % of aminoacetic acid and 13 wt % of hydrogen peroxide. Each of the resultant polishing solutions was used to polish a Cu film formed on a substrate and having projections following the same procedures as discussed earlier by using the polishing apparatus illustrated in FIG. 1. A list of the Cu film polishing rates of these polishing solutions is given in Table 1 below. Note that Table 1 also shows the polishing rate of a Cu film polished with a polishing solution added with no abrasive grains and containing 0.1 wt % of aminoacetic acid and 13 wt % of hydrogen peroxide.

TABLE 1

Type of abrasive grain	Polishing rate of Cu film (nm/min)
Silica grain	35.3
Alumina grain	98.5
Cerium oxide grain	31.1
Zirconia grain	22.1
None	10.0

As can be seen from Table 1 above, the polishing rate of a Cu film can be improved by the use of each polishing solution added with abrasive grains compared to the polishing solution added with no abrasive grains. It is also evident from Table 1 that the Cu film polishing rate can be controlled by changing the type of abrasive grain.

An SiO₂ film, an Si₃N₄ film, and a borophosphosilicate glass film (BPSG film) formed on substrates were polished following the same procedures as discussed earlier by using

polishing solutions added with silica grains and alumina grains as abrasive grains and the polishing apparatus illustrated in FIG. 1. Table 2 below shows the polishing rates of the individual insulating films obtained by these polishing solutions. Note that each value in parentheses in Table 2 indicates the velocity ratio calculated from (the polishing rate of a Cu film/the polishing rate of an insulating film in a polishing solution of the same type). In the manufacture of semiconductor devices to be described later, the selective polishing property for Cu can be improved as the velocity ratio is increased in forming a buried Cu interconnecting layer in a trench or the like of an insulating film by polishing. That is, a decrease in thickness of the underlying insulating film can be suppressed.

TABLE 2

Type of abrasive	Polishing rate of insulating film (nm/min)		
	SiO ₂ film	Si ₃ N ₄ film	BPSG film
grain			
Silica grain	1 (35.3)	0.4 (88.3)	4.7 (7.5)
Alumina grain	7.7 (12.8)	3.5 (28.1)	41.2 (2.39)

Furthermore, the polishing solution added with abrasive grains such as silica grains can perform polishing well without producing cracks or fine flaws on a Cu film or a Cu alloy film. This is so because, when the polishing step is performed by using the polishing apparatus shown in FIG. 1, the frictional force between the surface to be polished of a Cu film and the polishing pad can be reduced by the abrasive grains. This consequently reduces the impact force on the Cu film, preventing cracks and the like.

The polishing solution added with abrasive grains such as silica grains, therefore, can improve the polishing rate of Cu or a Cu alloy in comparison with a polishing solution added with no abrasive grains, and can also suppress damages to the surface of Cu or a Cu alloy during the polishing.

Note that a polishing solution containing amidosulfuric acid as an organic acid and abrasive grains such as silica grains also can improve the polishing rate of Cu or a Cu alloy compared to a polishing solution added with no abrasive grains, and can suppress damages to the surface of Cu or a Cu alloy during the polishing.

A method for manufacturing a semiconductor device according to the present invention comprises the steps of:

forming a trench and/or an opening corresponding to a shape of an interconnecting layer in an insulating film on a semiconductor substrate;

depositing an interconnection material film consisting of copper (Cu) or a copper alloy (Cu alloy) on the insulating film including the trench and/or opening; and

polishing the interconnection material film until a surface of the insulating film is exposed by using a polishing solution containing at least one organic acid selected from the group consisting of aminoacetic acid and amidosulfuric acid, an oxidizer, and water, thereby forming a buried interconnecting layer in the insulating film such that surfaces of the interconnecting layer and the insulating film are level with each other.

As the insulating film, it is possible to use, e.g., a silicon oxide film, a silicon nitride film, a two-layer film constituted by a silicon oxide film and a silicon nitride film stacked on the silicon oxide film, a borophosphosilicate glass film (BPSG film), or a phosphosilicate glass film (PSG film).

As the Cu alloy, it is possible to use, e.g., a Cu—Si alloy, a Cu—Al alloy, a Cu—Si—Al alloy, or a Cu—Ag alloy.

The interconnection material film consisting of Cu or a Cu alloy is deposited by sputter vapor deposition, vacuum vapor deposition, or the like.

It is preferable that the content of the organic acid and the content ratio of the organic acid to the oxidizer in the polishing solution fall within ranges identical with those of the copper-based metal polishing solution discussed above.

The polishing solution may contain an alkaline agent for adjusting the solution pH between 9 and 14, in addition to the organic acid and the oxidizer. Preferable examples of this alkaline agent are potassium hydroxide and quinoline.

The polishing solution may contain abrasive grains, such as silica grains, alumina grains, cerium oxide grains, or zirconia grains, in addition to the organic acid and the oxidizer. The mean grain size and the addition amount of these abrasive grains preferably fall within ranges identical with those of the copper-based metal polishing solution described above.

Polishing using the above polishing solution is performed by using the polishing apparatus explained earlier with reference to FIG. 1.

In the polishing using the polishing apparatus of FIG. 1, the load applied to a substrate held by the substrate holder toward the polishing pad is properly selected in accordance with the composition of a polishing solution. As an example, the load is preferably 200 to 2000 g/cm² for a polishing solution composed of an organic acid, an oxidizer, and water. The load is preferably 150 to 1000 g/cm² for a polishing solution further containing abrasive grains such as silica grains.

In the method for manufacturing a semiconductor device according to the present invention, a barrier layer may be formed on the insulating film formed on the semiconductor substrate and including the trench and/or opening prior to depositing the interconnection material film. With the formation of this barrier layer on the insulating film including the trench and/or opening, it is possible to form a buried interconnecting layer surrounded by the barrier layer by deposition and etch back of an interconnection material layer such as Cu. As a result, it is possible to prevent contamination of the semiconductor substrate caused by diffusion of Cu as the interconnection material layer.

The barrier layer consists of, e.g., TiN, Ti, Nb, W, or a CuTa alloy. The thickness of the barrier layer is preferably 15 to 50 nm.

In the method for manufacturing a semiconductor device according to the present invention, the end point of polishing may be detected on the basis of a change in the torque of the turntable of the polishing apparatus shown in FIG. 1, a change in the temperature of the polishing pad of the apparatus, or a change in the pH of the polishing solution supplied to the polishing pad. It is also possible to detect the end point of polishing on the basis of a change in the torque of the holder of the polishing apparatus in FIG. 1. The end point of the polishing can be detected easily with these methods. Therefore, a buried interconnecting layer can be reliably formed in the insulating film by using this end point detection.

In the method for manufacturing a semiconductor device according to the present invention as discussed above, a trench and/or an opening corresponding to an interconnecting layer is formed in an insulating film on a semiconductor substrate. An interconnection material film consisting of Cu or a Cu alloy is deposited on the insulating film including the trench and/or opening. The interconnection material film is polished until the surface of the insulating film is exposed by using a polishing solution containing at least one organic

acid selected from aminoacetic acid and amidosulfuric acid, an oxidizer, and water, and the polishing apparatus shown in FIG. 1. As has been discussed earlier, the polishing solution hardly etches a Cu film or a Cu alloy film when the film is dipped into the solution, and has an etching rate during polishing which is several times to several ten times higher than that during dipping. Consequently, in the polishing step the interconnection material film is sequentially etched from its surface, i.e., subjected to so-called etch back. This makes it possible to form a buried interconnecting layer consisting of Cu or a Cu alloy in the trench and/or opening in the insulating film such that the surface of the interconnecting layer is level with the surface of the insulating film. The interconnecting layer after etched back is brought into contact with the polishing solution. Since, however, an oxide layer is formed on the exposed surface of the interconnecting layer, it is possible to avoid etching of the interconnecting layer by this oxide layer. Therefore, a semiconductor device having a highly precise buried interconnecting layer and a flat surface can be manufactured.

Also, by adjusting the pH of the polishing solution between 9 and 14 with an alkaline agent such as potassium hydroxide, etching of the interconnecting layer after the etch-back step can be prevented by an oxide film which is formed on the surface of the interconnecting layer and has a good etching barrier property, even if the amount of the organic acid, such as aminoacetic acid, contained in the polishing solution is increased. In addition, increasing the content of the organic acid in the polishing solution increases the polishing rate of the interconnection material film. As a result, the etch-back time can be shortened.

Furthermore, the use of a polishing solution added with abrasive grains such as silica grains makes it possible to raise the polishing rate of the interconnection material layer. This also reduces the etch-back time. It is also possible to discourage occurrence of cracks or flaws on the interconnection material film in the etch-back step. Consequently, a highly reliable buried interconnecting layer can be formed in the trench and/or opening of the insulating film.

Another method for manufacturing a semiconductor device according to the present invention comprises the steps of:

forming a trench and/or an opening corresponding to a shape of an interconnecting layer in an insulating film on a semiconductor substrate;

depositing an interconnection material film consisting of copper (Cu) or a copper alloy (Cu alloy) on the insulating film including the trench and/or opening;

polishing the interconnection material film until a surface of the insulating film is exposed by using a polishing solution containing at least one type of an organic acid selected from the group consisting of aminoacetic acid and amidosulfuric acid, an oxidizer, and water, thereby forming a buried interconnecting layer in the insulating film such that surfaces of the interconnecting layer and the insulating film are level with each other; and

treating the surface of the insulating film including the interconnecting layer with an aqueous dissolved ozone solution and then with an aqueous dilute hydrofluoric acid solution.

As the insulating film, it is possible to use, e.g., a silicon oxide film, a silicon nitride film, a two-layer film constituted by a silicon oxide film and a silicon nitride film stacked on the silicon oxide film, a borophosphosilicate glass film (BPSG film), or a phosphosilicate glass film (PSG film).

As the Cu alloy, it is possible to use, e.g., a Cu—Si alloy, a Cu—Al alloy, a Cu—Si—Al alloy, or a Cu—Ag alloy.

The interconnection material film consisting of Cu or a Cu alloy is deposited by sputter vapor deposition, vacuum vapor deposition, or the like process.

It is preferable that the content of an organic acid and the content ratio of the organic acid to an oxidizer in the polishing solution fall within ranges identical with those of the copper-based metal polishing solution discussed above.

The polishing solution may contain an alkaline agent for adjusting the solution pH between 9 and 14, in addition to the organic acid and the oxidizer. Preferable examples of this alkaline agent are potassium hydroxide and quinoline.

The polishing solution may contain abrasive grains, such as silica grains, alumina grains, cerium oxide grains, or zirconia grains, in addition to the organic acid and the oxidizer. The mean grain size and the addition amount of these abrasive grains preferably fall within ranges identical with those of the copper-based metal polishing solution described above.

Polishing using the above polishing solution is performed by using the polishing apparatus explained earlier with reference to FIG. 1.

In the polishing using the polishing apparatus of FIG. 1, the load applied to a substrate held by the substrate holder toward the polishing pad is properly selected in accordance with the composition of a polishing solution. As an example, the load is preferably 200 to 2000 g/cm² for a polishing solution composed of an organic acid, an oxidizer, and water. The load is preferably 150 to 1000 g/cm² for a polishing solution further containing abrasive grains such as silica grains.

In this method for manufacturing of a semiconductor device according to the present invention, a barrier layer may be formed on the insulating film formed on the semiconductor substrate and including the trench and/or opening prior to depositing the interconnection material film. With the formation of this barrier layer on the insulating film including the trench and/or opening, it is possible to form a buried interconnecting layer surrounded by the barrier layer by deposition and etch back of an interconnection material layer such as Cu. As a result, it is possible to prevent contamination of the semiconductor substrate caused by diffusion of Cu as the interconnection material layer.

The barrier layer consists of, e.g., TiN, Ti, Nb, W, or a CuTa alloy. The thickness of the barrier layer is preferably 15 to 50 nm.

In this method for manufacturing a semiconductor device according to the present invention, the end point of polishing may be detected on the basis of a change in the torque of the turntable of the polishing apparatus shown in FIG. 1, a change in the temperature of the polishing pad of the apparatus, or a change in the pH of the polishing solution supplied to the polishing pad. It is also possible to detect the end point of polishing on the basis of a change in the torque of the holder of the polishing apparatus in FIG. 1. The end point of the polishing can be detected easily with these methods. Therefore, a buried interconnecting layer can be reliably formed in the insulating film by using this end point detection.

The ozone concentration of the aqueous dissolved ozone solution is preferably 0.1 to 25 ppm. If the ozone concentration of the aqueous dissolved ozone solution is smaller than 0.1 ppm, it becomes difficult to convert Cu or a Cu alloy, as the interconnection material remaining on the insulating film, into an oxide, or to oxidatively destroy a contaminant such as an organic substance. The ozone concentration of the aqueous dissolved ozone solution is more preferably 5 to 25 ppm.

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The hydrofluoric acid concentration of the aqueous dilute hydrofluoric acid solution is preferably 0.05 to 20%. If the hydrofluoric acid concentration of the aqueous dilute hydrofluoric acid solution is less than 0.05%, it becomes difficult to effectively dissolve away the oxide of the Cu or Cu alloy which is converted by the treatment using the aqueous dissolved ozone solution. On the other hand, if the hydrofluoric acid concentration of the aqueous dilute hydrofluoric acid solution is more than 20%, when a silicon oxide film is used as an insulating film, this oxide film also may be removed by dissolution to cause a decrease in the film thickness. The hydrofluoric acid concentration of the aqueous dilute hydrofluoric acid solution is more preferably 0.1 to 5%.

In this method for manufacturing a semiconductor device according to the present invention as discussed above, a trench and/or an opening corresponding to an interconnecting layer is formed in an insulating film on a semiconductor substrate. An interconnection material film consisting of Cu or a Cu alloy is deposited on the insulating film including the trench and/or opening. The interconnection material film is polished until the surface of the insulating film is exposed by using a polishing solution containing at least one organic acid selected from aminoacetic acid and amidosulfuric acid, an oxidizer, and water, and the polishing apparatus shown in FIG. 1. As has been discussed earlier, the polishing solution hardly etches a Cu film or a Cu alloy film when the film is dipped into the solution, and has an etching rate during polishing which is several times to several ten times higher than that during dipping. Consequently, in the polishing step the interconnection material film is sequentially etched from its surface, i.e., subjected to so-called etch back. This makes it possible to form a buried interconnecting layer consisting of Cu or a Cu alloy in the trench and/or opening in the insulating film such that the surface of the interconnecting layer is level with the surface of the insulating film. The interconnecting layer after etched back is brought into contact with the polishing solution. Since, however, an oxide layer is formed on the exposed surface of the interconnecting layer, it is possible to avoid etching of the interconnecting layer by this oxide layer.

In addition, by treating the surface of the insulating film including the interconnecting layer with the aqueous dissolved ozone solution after the etch-back step, it is possible to convert a fine interconnection material, i.e., Cu or a Cu alloy, remaining on the insulating film into an oxide, or to oxidatively destroy a pollutant such as an organic substance. By performing a treatment with the aqueous dilute hydrofluoric acid solution after the treatment using the aqueous dissolved ozone solution, it is possible to readily dissolve away the oxide of the Cu or Cu alloy from the insulating film or the oxidatively destroyed product of the pollutant.

Consequently, it is possible to manufacture a semiconductor device having a highly precise buried interconnecting layer and a flat surface which is cleaned by removing an organic substance or the residual interconnection material from the surface of an insulating film.

Also, by adjusting the pH of the polishing solution between 9 and 14 with an alkaline agent such as potassium hydroxide, etching of the interconnecting layer after the etch-back step can be prevented by an oxide film which is formed on the surface of the interconnecting layer and has a good etching barrier property, even if the amount of the organic acid, such as aminoacetic acid, contained in the polishing solution is increased. In addition, increasing the content of the organic acid in the polishing solution increases the polishing rate of the interconnection material film. As a result, the etch-back time can be shortened.

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Furthermore, the use of a polishing solution added with abrasive grains such as silica grains makes it possible to raise the polishing rate of the interconnection material layer. This also reduces the etch-back time. It is also possible to discourage occurrence of cracks or flaws on the interconnection material film in the etch-back step. Consequently, a highly reliable buried interconnecting layer can be formed in the trench and/or opening of the insulating film.

The present invention will be described in more detail below by way of its preferred examples.

EXAMPLE 1

First, as in FIG. 8A, a 1000 nm thick SiO_2 film 22 as an insulating interlayer was deposited by a CVD process on a silicon substrate 21 on the surface of which diffusion layers such as a source and a drain (not shown) were formed. Thereafter, a plurality of trenches 23, 500 nm in depth, having a shape corresponding to an interconnecting layer were formed in the SiO_2 film 22 by photoetching. As shown in FIG. 8B, a 15 nm thick TiN barrier layer 24 and a 600 nm thick Cu film 25 were deposited in this order by sputter vapor deposition on the SiO_2 film 22 including the trenches 23.

Subsequently, the substrate 21, FIG. 8B, was held upside down by the substrate holder 5 of the polishing apparatus discussed earlier with reference to FIG. 1. A load of 300 g/cm² was applied from the support shaft 4 of the holder 5 to the substrate toward the polishing pad 2 which was covered on the turntable 1 and consisted of SUBA800 (tradename) manufactured by Rodel Nitua Corp. While the turntable 1 and the holder 5 were rotated in the opposite directions at a rotating speed of 100 ppm, a polishing solution was supplied from the supply pipe 3 to the polishing pad 2 at a rate of 20 ml/min, thereby polishing the Cu film 25 and the barrier layer 24 deposited on the substrate 21 until the surface of the SiO_2 film 22 was exposed. Note that the polishing solution used was pure water containing 0.1 wt % of aminoacetic acid, 13.0 wt % of hydrogen peroxide, and 8 wt % of a silica powder with a mean grain size of 0.04 μm , in which the weight ratio of aminoacetic acid to hydrogen peroxide was 1 to 130. In the polishing step described above, the etching rate of the polishing solution when the solution was in contact with the Cu film was zero, and the etching rate during the polishing performed by the polishing pad was about 77 nm/min, which was sufficiently higher than that during the dipping. Consequently, in the polishing step the Cu film 25 with projections as in FIG. 8B was preferentially polished from the surface in mechanically contact with the polishing pad, and the exposed barrier layer 24 was then polished; i.e., so-called etch back was performed. As a result, as illustrated in FIG. 8C, the barrier layer 24 was left behind only in the trenches 23, and a buried Cu interconnecting layer 26 whose surface was level with the surface of the SiO_2 film 22 was formed in the trenches 23 covered with the barrier layer 24. After the load applied from the holder 5 of the polishing apparatus to the polishing pad 2 was removed and the rotations of the turntable 1 and the holder 5 were stopped, no etching proceeded even when the Cu interconnecting layer 26 came into contact with the polishing solution.

In the polishing step (etch-back step) performed by the polishing apparatus shown in FIG. 1, the polishing solution was sampled at proper intervals from the polishing pad, and a change in the pH of the solution was measured with a pH meter. FIG. 9 shows the pH change of the polishing solution as a function of the polishing time. In FIG. 9, a point at

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which the pH which once had declined started to rise again is defined as the etching end point (e.g., 8 minutes after the loading from the holder to the substrate was started). By setting the etch-back time on the basis of this end point detection, it was possible to form a buried Cu interconnecting layer 26, the surface of which was level with the surface of the SiO₂ film 22, in the trenches 23 of the film 22 with a high reproducibility.

In the polishing step (etch-back step) done by the polishing apparatus illustrated in FIG. 1, a change in the temperature of the polishing pad was measured by a temperature sensor, and a change in the voltage of a driving motor of the turntable was also measured. FIG. 10 shows the temperature change of the polishing pad as a function of the polishing time. FIG. 11 shows the voltage change of the driving motor as a function of the polishing time. In FIG. 10 illustrating the temperature change, a point at which the temperature of the polishing pad, which had risen to a constant temperature immediately after the start of loading, started to rise again is defined as the etching end point. In FIG. 11 showing the voltage change, a point at which the voltage of the driving motor of the turntable, which had risen to a fixed voltage immediately after the start of loading, started to rise again is defined as the etching end point. By setting the etch-back time on the basis of these end point detections, it was possible to form with a high reproducibility a buried Cu interconnecting layer 26, the surface of which was level with the surface of the SiO₂ film 22, in the trenches 23 of the film 22.

The substrate in which the buried interconnecting layer was formed was treated by dipping into an aqueous dissolved ozone solution with an ozone concentration of 0.001% for 3 minutes. The substrate was then treated by dipping into an aqueous dilute hydrofluoric acid solution with a hydrofluoric acid concentration of 10% for 90 seconds. FIG. 12 is a graph showing spectra analyzed by XPS. In FIG. 12, the solid line indicates a spectrum of the surface immediately after the formation of the Cu interconnecting layer; the dotted line, a spectrum of the surface of the Cu interconnecting layer after the treatment with the aqueous dissolved ozone solution; and the alternate long and short dashed line, a spectrum of the surface of the Cu interconnecting layer after the treatment with the aqueous dilute hydrofluoric acid solution. As is apparent from FIG. 12, when the substrate in which the interconnection was formed was treated by dipping into the aqueous dissolved ozone solution, a signal of metal Cu that was observed immediately after the formation of the interconnection was no longer found, as indicated by the dotted-line spectrum. This indicates that the surface of the Cu interconnecting layer changed into an oxide. When the substrate was further treated with the aqueous dilute hydrofluoric acid solution, a signal of CuO that was observed in the treatment with the aqueous dissolved ozone solution disappeared, as shown by the spectrum represented by the alternate long and short dashed line. This demonstrates that pure Cu was exposed to the surface of the Cu interconnecting layer. That is, the treatment using the aqueous dissolved ozone solution makes it possible to destroy an organic substance, such as aminoacetic acid, remaining on the surface of the SiO₂ film 22 or the like, and to convert the residual Cu on the SiO₂ film 22 into an oxide. The destroyed product of the organic substance and the Cu oxide formed by the treatment using the aqueous dissolved ozone solution can be removed by the subsequent treatment using the aqueous dilute hydrofluoric acid solution. It is also possible to remove the Cu oxide layer formed on the surface of the Cu interconnecting layer by

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contact with the polishing solution. Consequently, the surface of the SiO₂ film 22 can be cleaned, and pure Cu can be exposed to the surface of the Cu interconnecting layer 26.

In Example 1 of the present invention, therefore, a buried Cu interconnecting layer 26 having a thickness equal to the depth of the trenches 23 of the SiO₂ film 22 can be formed in the trenches 23 such that the surface of the Cu interconnecting layer 26 is level with the surface of the SiO₂ film 22. This makes it possible to flatten the surface of the substrate 21 after the formation of the interconnecting layer 26. Additionally, by performing the treatment using the aqueous dissolved ozone solution and the treatment using the aqueous dilute hydrofluoric acid solution after the formation of the Cu interconnecting layer 26, the surface of the SiO₂ film 22 is cleaned, and the oxide layer which is produced by oxidation by the polishing solution and serves as a resistive component is removed. Consequently, it is possible to manufacture a semiconductor device which has a buried Cu interconnecting layer with a low resistance characteristic of Cu and which is highly reliable.

Note that the same procedures as discussed above in Example 1 were also followed by using a polishing solution which was pure water containing 0.86 wt % of amidosulfuric acid, 30 wt % of hydrogen peroxide, and 8 wt % of a silica powder with a mean grain size of 0.09 μ m. As a result, as in Example 1, it was possible to form a buried interconnecting layer in trenches of an SiO₂ insulating interlayer such that the surfaces of the interconnecting layer and the SiO₂ film were level with each other.

EXAMPLE 2

First, as in FIG. 13A, an 800 nm thick SiO₂ film 22 and a 200 nm thick Si₃N₄ film 27 were deposited in this order to form an insulating interlayer by a CVD process on a silicon substrate 21 on the surface of which diffusion layers such as a source and a drain (not shown) were formed. Thereafter, a plurality of trenches 23, 500 nm in depth, having a shape corresponding to an interconnecting layer were formed in the Si₃N₄ film 27 and the SiO₂ film 22 by photoetching. As shown in FIG. 13B, a 15 nm thick TiN barrier layer 24 and a 600-nm thick Cu film 25 were deposited in this order by sputter vapor deposition on the Si₃N₄ film 27 including the trenches 23.

Subsequently, the substrate 21, FIG. 13B, was held upside down by the substrate holder 5 of the polishing apparatus discussed earlier with reference to FIG. 1. A load of 300 g/cm² was applied from the support shaft 4 of the holder 5 to the substrate toward the polishing pad 2 which was covered on the turntable 1 and consisted of SUBA800 (tradename) manufactured by Rodex Nitta Corp. While the turntable 1 and the holder 5 were rotated in the opposite directions at a rotating speed of 100 ppm, a polishing solution was supplied from the supply pipe 3 to the polishing pad 2 at a rate of 20 ml/min, thereby polishing the Cu film 25 and the barrier layer 24 deposited on the substrate 21 until the surface of the Si₃N₄ film 27 was exposed. Note that the polishing solution used was pure water containing 0.1 wt % of aminoacetic acid, 13.0 wt % of hydrogen peroxide, and 8 wt % of a silica powder with a mean grain size of 0.04 μ m, in which the weight ratio of aminoacetic acid to hydrogen peroxide was 1 to 130. In the polishing step described above, the etching rate of the polishing solution when the solution was in contact with the Cu film was zero, and the etching rate during the polishing performed by the polishing pad was about 77 nm/min, which was sufficiently higher than that

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during the dipping. Consequently, in the polishing step the Cu film 25 with projections as in FIG. 13B was preferentially polished from the surface in mechanically contact with the polishing pad, and the exposed barrier layer 24 was then polished; i.e., so-called etch back was performed.

As a result, as illustrated in FIG. 13C, the barrier layer 24 was left behind only in the trenches 23, and a buried Cu interconnecting layer 26 whose surface was level with the surface of the Si_3N_4 film 27 was formed in the trenches 23 covered with the barrier layer 24. After the load applied from the holder 5 of the polishing apparatus to the polishing pad 2 was removed and the rotations of the turntable 1 and the holder 5 were stopped, no etching proceeded even when the Cu interconnecting layer 26 came into contact with the polishing solution.

Furthermore, since the Si_3N_4 film 27 exhibiting a high polishing resistance in the polishing step using the polishing solution containing the silica grains as abrasive grains was formed on the surface of the insulating interlayer, it was possible to suppress a decrease in the film thickness in the etch-back step. This made it possible to manufacture a semiconductor device including an insulating interlayer with a high withstand voltage.

EXAMPLE 3

First, as in FIG. 14A, a 1000 nm thick Si_3N_4 film 27 as an insulating interlayer was deposited by a CVD process on a silicon substrate 21 on the surface of which diffusion layers such as a source and a drain (not shown) were formed. Thereafter, a plurality of trenches 23, 500 nm in depth, having a shape corresponding to an interconnecting layer were formed in the Si_3N_4 film 27 by photoetching. As shown in FIG. 14B, a 600 nm thick Cu film 25 was deposited on the Si_3N_4 film 27 including the trenches 23 by sputter vapor deposition.

Subsequently, the substrate 21, FIG. 14B, was held upside down by the substrate holder 5 of the polishing apparatus discussed earlier with reference to FIG. 1. A load of 400 g/cm² was applied from the support shaft 4 of the holder 5 to the substrate toward the polishing pad 2 which was covered on the turntable 1 and consisted of SUBA800 (tradename) manufactured by Rodel Nitta Corp. While the turntable 1 and the holder 5 were rotated in the opposite directions at a rotating speed of 100 ppm, a polishing solution was supplied from the supply pipe 3 to the polishing pad 2 at a rate of 20 ml/min, thereby polishing the Cu film 25 deposited on the substrate 21 until the surface of the Si_3N_4 film 27 was exposed. Note that the polishing solution used was pure water containing 0.9 wt % of aminoacetic acid, 22.0 wt % of hydrogen peroxide, and 3.7 wt % of potassium hydroxide, in which the weight ratio of aminoacetic acid to hydrogen peroxide was 1 to about 24 and the pH was 10.5. In the polishing step described above, the etching rate of the polishing solution when the solution was in contact with the Cu film was zero, and the etching rate during the polishing performed by the polishing pad was about 220 nm/min, which was sufficiently higher than that during the dipping. Consequently, in the polishing step the Cu film 25 with projections as in FIG. 14B was preferentially polished from the surface in mechanically contact with the polishing pad, i.e., subjected to so-called etch back.

As a result, as illustrated in FIG. 14C, a buried Cu interconnecting layer 26 whose surface was level with the surface of the Si_3N_4 film 27 was formed in the trenches 23. After the load applied from the holder 5 of the polishing

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apparatus to the polishing pad 2 was removed and the rotations of the turntable 1 and the holder 5 were stopped, no etching proceeded even when the Cu interconnecting layer 26 came into contact with the polishing solution.

Furthermore, the insulating interlayer having the trenches 23 in which the buried Cu interconnecting layer 26 was formed was constructed from Si_3N_4 with a good Cu diffusion barrier property. Therefore, since Cu did not diffuse across the insulating interlayer 27 to reach the silicon substrate 21 from the Cu interconnecting layer 26, it was possible to avoid contamination of the substrate 21 without forming any barrier layer such as a TiN layer on the inner surfaces of the trenches 23.

EXAMPLE 4

First, as in FIG. 15A, a 1000 nm thick SiO_2 film 33 as a first insulating interlayer was deposited by a CVD process on a p-type silicon substrate 32 on the surface of which an n^+ -type diffusion layer 31 was formed. Thereafter, a via hole 34 was formed in a portion of the SiO_2 film 33 corresponding to the diffusion layer 31 by photoetching. As shown in FIG. 15B, a 20 nm thick TiN barrier layer 35 was deposited on the SiO_2 film 33 including the via hole 34 by sputter vapor deposition, and a 1100 nm thick Cu film 36 was then deposited by sputter vapor deposition.

Subsequently, the substrate 32, FIG. 15B, was held upside down by the substrate holder 5 of the polishing apparatus discussed earlier with reference to FIG. 1. A load of 300 g/cm² was applied from the support shaft 4 of the holder 5 to the substrate toward the polishing pad 2 which was covered on the turntable 1 and consisted of SUBA800 (tradename) manufactured by Rodel Nitta Corp. While the turntable 1 and the holder 5 were rotated in the opposite directions at a rotating speed of 100 ppm, a polishing solution was supplied from the supply pipe 3 to the polishing pad 2 at a rate of 20 ml/min, thereby polishing the Cu film 36 and the barrier layer 35 deposited on the substrate 32 until the surface of the SiO_2 film 33 was exposed. Note that the polishing solution used was pure water containing 0.2 wt % of aminoacetic acid, 20.0 wt % of hydrogen peroxide, and 10 wt % of a silica powder with a mean grain size of 0.04 μm , in which the weight ratio of aminoacetic acid to hydrogen peroxide was 1 to 100. In the polishing step described above, the etching rate of the polishing solution when the solution was in contact with the Cu film was zero, and the etching rate during the polishing performed by the polishing pad was about 70 nm/min, which was sufficiently higher than that during the dipping. Consequently, in the polishing step the Cu film 36 with projections as in FIG. 15B was preferentially polished from the surface in mechanically contact with the polishing pad, and the exposed barrier layer 35 was then polished; i.e., so-called etch back was performed. As a result, as illustrated in FIG. 15C, the barrier layer 35 was left behind only in the via hole 34, and a Cu via fill 37 whose surface was level with the surface of the SiO_2 film 33 was formed in the via hole 34 covered with the barrier layer 35. After the load applied from the holder 5 of the polishing apparatus to the polishing pad 2 was removed and the rotations of the turntable 1 and the holder 5 were stopped, no etching proceeded even when the Cu via fill 37 was brought into contact with the polishing solution. Subsequently, the substrate in which the via fill 37 was formed was treated by dipping into an aqueous dissolved ozone solution with an ozone concentration of 0.002% for 3 minutes, and then treated by dipping into an aqueous dilute hydrofluoric acid

solution with a hydrofluoric acid concentration of 5% for 9 seconds, thereby cleaning the surface of the SiO_2 film 33.

Subsequently, as in FIG. 15D, an 800 nm thick Si_3N_4 film 38 as a second insulating interlayer was deposited by a CVD process on the SiO_2 film 33 including the via fill 37. Thereafter, a plurality of trenches 39, 400 nm in depth, having a shape corresponding to an interconnecting layer were formed in the Si_3N_4 film 38 by photoetching. In addition, a through hole 40 was formed in the trench 39 located on the via fill 37 by photoetching. As shown in FIG. 15E, a 900 nm thick Cu film 41 was deposited on the Si_3N_4 film 38 including the trenches 39 and the through hole 40 by sputter vapor deposition.

Subsequently, the substrate 32, FIG. 15E, was held upside down by the substrate holder 5 of the polishing apparatus discussed earlier with reference to FIG. 1. A load of 300 g/cm² was applied from the support shaft 4 of the holder 5 to the substrate toward the polishing pad 2 which was covered on the turntable 1 and consisted of SUBA800 (tradename) manufactured by Rodel Nitta Corp. While the turntable 1 and the holder 5 were rotated in the opposite directions at a rotating speed of 100 ppm, a polishing solution of the composition identical with that used in the etch-back step described above was supplied from the supply pipe 3 to the polishing pad 2 at a rate of 20 ml/min, thereby polishing the Cu film 41 deposited on the substrate 32 until the surface of the Si_3N_4 film 38 was exposed. Consequently, the Cu film 41 with projections as in FIG. 15E was preferentially polished from the surface in mechanically contact with the polishing pad, i.e., subjected to so-called etch back. By this etch back, a buried Cu interconnecting layer 42 whose surface was level with the surface of the Si_3N_4 film 38 was formed in the trenches 39, as illustrated in FIG. 15F. Simultaneously, a buried Cu interconnecting layer 42 connected to the via fill 37 through the through hole 40 was also formed. After the load applied from the holder 5 of the polishing apparatus to the polishing pad 2 was removed and the rotations of the turntable 1 and the holder 5 were stopped, no etching proceeded even when the Cu interconnecting layer 42 came into contact with the polishing solution.

In Example 4 of the present invention, therefore, it was possible to manufacture a semiconductor device which had a multilayer interconnecting structure including the first and second insulating interlayers 33 and 38, the via fill 37 formed in the first insulating interlayer 33 and having a surface level with the surface of the first insulating interlayer 33, and the Cu interconnecting layer 42 formed in the second insulating interlayer 38 and having a surface level with the second insulating interlayer 38, and which also had a flat surface.

According to the present invention as has been discussed above, it is possible to provide a copper-based metal polishing solution which hardly etches Cu or Cu alloy when Cu or a Cu alloy is dipped into the solution, and has an etching rate during polishing several times to several ten times higher than that during dipping.

According to the present invention, it is also possible to provide a method for manufacturing a semiconductor device with a flat surface, in which a trench and/or an opening is formed in an insulating film on a semiconductor substrate, an interconnection material film deposited on the insulating film and consisting of Cu or a Cu alloy can be etched back within a short time period, and consequently a buried interconnecting layer consisting of Cu or a Cu alloy is formed in the insulating film such that the surface of the

interconnecting layer is level with the surface of the insulating film.

Furthermore, according to the present invention, it is possible to provide a method for manufacturing a semiconductor device, in which a trench and/or an opening is formed in an insulating film on a semiconductor substrate, and an interconnection material film deposited on the insulating film and consisting of Cu or a Cu alloy can be etched back within a short time period to form a buried interconnecting layer whose surface is level with the surface of the insulating film, and which has a clean, flat surface obtained by removing an organic substance or the residual interconnection material from the surface of the insulating film after the etch back.

Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details, representative devices, and illustrated examples shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.

What is claimed is:

1. A copper-based metal polishing solution containing at least one organic acid selected from the group consisting of aminoacetic acid and amidosulfuric acid, an oxidizer, and water.
2. The polishing solution according to claim 1, wherein said oxidizer is hydrogen peroxide.
3. The polishing solution according to claim 1, wherein said organic acid is contained in an amount of 0.01 to 10 wt % in said polishing solution, and a content ratio of said organic acid to said oxidizer is 1 to not less than 20 as a weight ratio.
4. The polishing solution according to claim 3, wherein said organic acid is contained in an amount of 0.01 to 1 wt % in said polishing solution.
5. The polishing solution according to claim 3, wherein the content ratio of said organic acid to said oxidizer is 1 to not less than 40 as a weight ratio.
6. The polishing solution according to claim 3, wherein said oxidizer is contained in an amount of a maximum of 30 wt % in said polishing solution.
7. The polishing solution according to claim 1, further containing an alkaline agent for adjusting a pH of the solution between 9 and 14.
8. The polishing solution according to claim 7, wherein said alkaline agent is potassium hydroxide.
9. The polishing solution according to claim 7, wherein said alkaline agent is quinoline.
10. The polishing solution according to claim 1, further containing abrasive grains.
11. The polishing solution according to claim 10, wherein said abrasive grain is made of at least one material selected from the group consisting of silica, zirconia, cerium oxide, and alumina.
12. The polishing solution according to claim 10, wherein said abrasive grains have a mean grain size of 0.02 to 0.1 μm .
13. The polishing solution according to claim 10, wherein said abrasive grains are contained in an amount of 1 to 14 wt % in said polishing solution.
14. The polishing solution according to claim 10, wherein said abrasive grains are contained in an amount of 3 to 10 wt % in said polishing solution.
15. A method for manufacturing a semiconductor device, comprising the steps of:

forming at least one member selected from the group consisting of a trench and an opening corresponding to a shape of an interconnecting layer in an insulating film on a semiconductor substrate;

depositing an interconnection material film consisting of copper or a copper alloy on said insulating film including said at least one member selected from the group consisting of a trench and an opening; and

polishing said interconnection material film until a surface of said insulating film is exposed by using a polishing solution containing at least one organic acid selected from the group consisting of aminoacetic acid and amidosulfuric acid, an oxidizer, and water, thereby forming a buried interconnecting layer in said insulating film such that surfaces of said interconnecting layer and said insulating film are level with each other.

16. The method according to claim 15, wherein said insulating film is a silicon oxide film.

17. The method according to claim 15, wherein said insulating film has a two-layer structure constituted by a silicon oxide film and a silicon nitride film formed on said silicon oxide film.

18. The method according to claim 15, wherein a barrier layer is formed on said insulating film including said at least one member selected from the group consisting of a trench and an opening prior to depositing said interconnection material film.

19. The method according to claim 18, wherein said barrier layer is made of one material selected from the group consisting of TiN, Ti, Nb, W, and a CuTa alloy.

20. The method according to claim 19, wherein said barrier layer has a thickness of 15 to 50 nm.

21. The method according to claim 15, wherein said Cu alloy is one material selected from the group consisting of a Cu—Si alloy, a Cu—Al alloy, a Cu—Si—Al alloy, and a Cu—Ag alloy.

22. The method according to claim 15, wherein said oxidizer is hydrogen peroxide.

23. The method according to claim 15, wherein said organic acid is contained in an amount of 0.01 to 10 wt % in said polishing solution, and a content ratio of said organic acid to said oxidizer is 1 to not less than 20 as a weight ratio.

24. The method according to claim 23, wherein said organic acid is contained in an amount of 0.01 to 1 wt % in said polishing solution.

25. The method according to claim 23, wherein the content ratio of said organic acid to said oxidizer is 1 to not less than 40 as a weight ratio.

26. The method according to claim 23, wherein said oxidizer is contained in an amount of a maximum of 30 wt % in said polishing solution.

27. The method according to claim 15, wherein said polishing solution further contains an alkaline agent for adjusting a pH of the solution between 9 and 14.

28. The method according to claim 27, wherein said alkaline agent is potassium hydroxide.

29. The method according to claim 27, wherein said alkaline agent is quinoline.

30. The method according to claim 15, wherein said polishing solution further contains abrasive grains.

31. The method according to claim 30, wherein said abrasive grain is made of at least one material selected from the group consisting of silica, zirconia, cerium oxide, and alumina.

32. The method according to claim 30, wherein said abrasive grains have a mean grain size of 0.02 to 0.1 μm .

33. The method according to claim 30, wherein said abrasive grains are contained in an amount of 1 to 14 wt % in said polishing solution.

34. The method according to claim 30, wherein said abrasive grains are contained in an amount of 3 to 10 wt % in said polishing solution.

35. The method to claim 15, wherein the polishing is performed by using apparatus comprising a turntable covered with a polishing pad, means for supplying said polishing solution to said polishing pad of said turntable, and a substrate holder which holds said semiconductor substrate on a lower surface thereof and rotates said substrate while pressing said substrate against said polishing pad.

36. The method according to claim 35, wherein an end point of the polishing is detected on the basis of a change in torque of said turntable of said polishing apparatus.

37. The method to claim 35, wherein an end point of the polishing is detected on the basis of a change in temperature of said polishing pad.

38. The method according to claim 35, wherein an end point of the polishing is detected on the basis of a change in pH of said polishing solution supplied to said polishing pad.

39. A method for manufacturing a semiconductor device, comprising the steps of:

forming at least one member selected from the group consisting of a trench and an opening corresponding to a shape of an interconnecting layer in an insulating film on a semiconductor substrate;

depositing an interconnection material film consisting of copper or a copper alloy on said insulating film including said at least one member selected from the group consisting of a trench and an opening;

polishing said interconnection material film until a surface of said insulating film is exposed by using a polishing solution containing at least one organic acid selected from the group consisting of aminoacetic acid and amidosulfuric acid, an oxidizer, and water, thereby forming a buried interconnecting layer in said insulating film such that surfaces of said interconnecting layer and said insulating film are level with each other; and

treating the surface of said insulating film including said interconnecting layer with an aqueous dissolved ozone solution and then with an aqueous dilute hydrofluoric acid solution.

40. The method according to claim 39, wherein said insulating film is a silicon oxide film.

41. The method according to claim 39, wherein said insulating film has a two-layer structure constituted by a silicon oxide film and a silicon nitride film formed on said silicon oxide film.

42. The method according to claim 39, wherein a barrier layer is formed on said insulating film including said at least one member selected from the group consisting of a trench and an opening prior to depositing said interconnection material film.

43. The method according to claim 42, wherein said barrier layer is made of one material selected from the group consisting of TiN, Ti, Nb, W, and a CuTa alloy.

44. The method according to claim 42, wherein said barrier layer has a thickness of 15 to 50 nm.

45. The method according to claim 39, wherein said Cu alloy is one material selected from the group consisting of a Cu—Si alloy, a Cu—Al alloy, a Cu—Si—Al alloy, and a Cu—Ag alloy.

46. The method according to claim 39, wherein said oxidizer is hydrogen peroxide.

47. The method according to claim 39, wherein said organic acid is contained in an amount of 0.01 to 10 wt % in said polishing solution, and a content ratio of said organic acid to said oxidizer is 1 to not less than 20 as a weight ratio.

48. The method according to claim 47, wherein said organic acid is contained in an amount of 0.01 to 1 wt % in said polishing solution.

49. The method according to claim 47, wherein the content ratio of said organic acid to said oxidizer is 1 to not less than 40 as a weight ratio.

50. The method according to claim 47, wherein said oxidizer is contained in an amount of a maximum of 30 wt % in said polishing solution.

51. The method according to claim 39, wherein said polishing solution further contains an alkaline agent for adjusting a pH of the solution between 9 and 14.

52. The method according to claim 51, wherein said alkaline agent is potassium hydroxide.

53. The method according to claim 51, wherein said alkaline agent is quinoline.

54. The method according to claim 39, wherein said polishing solution further contains abrasive grains.

55. The method according to claim 54, wherein said abrasive grain is made of at least one material selected from the group consisting of silica, zirconia, cerium oxide, and alumina.

56. The method according to claim 54, wherein said abrasive grains have a mean grain size of 0.02 to 0.1 μm .

57. The method according to claim 54, wherein said abrasive grains are contained in an amount of 1 to 14 wt % in said polishing solution.

58. The method according to claim 54, wherein said abrasive grains are contained in an amount of 3 to 10 wt % in said polishing solution.

59. The method according to claim 39, wherein the polishing is performed by using a polishing apparatus comprising a turntable covered with a polishing pad, means for supplying said polishing solution to said polishing pad of said turntable, and a substrate holder which holds said semiconductor substrate on a lower surface thereof and rotates said substrate while pressing said substrate against said polishing pad.

60. The method according to claim 59, wherein an end point of the polishing is detected on the basis of a change in torque of said turntable of said polishing apparatus.

61. The method according to claim 59, wherein an end point of the polishing is detected on the basis of a change in temperature of said polishing pad.

62. The method according to claim 59, wherein an end point of the polishing is detected on the basis of a change in pH of said polishing solution supplied to said polishing pad.

63. The method according to claim 39, wherein said aqueous dissolved ozone solution has an ozone concentration of 0.1 to 25 ppm.

64. The method according to claim 39, wherein said aqueous dissolved ozone solution has an ozone concentration of 5 to 25 ppm.

65. The method according to claim 39, wherein said aqueous dilute hydrofluoric acid solution has a hydrofluoric acid concentration of 0.05 to 20%.

66. The method according to claim 39, wherein said aqueous dilute hydrofluoric acid solution has a hydrofluoric acid concentration of 0.1 to 5%.

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[54] **ABRASIVE COMPOSITION FOR MAGNETIC
RECORDING DISC SUBSTRATE**

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106/11; 438/693

[58] **Field of Search** 51/306, 309; 106/3,
106/11; 438/693

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[57] **ABSTRACT**

An abrasive composition for polishing a substrate for a magnetic recording disc is described, which comprises finely divided zirconium oxide particles, an abrasion promoter, an optional water-soluble oxidizing agent, and water. This abrasive composition is used for polishing a substrate for a magnetic recording disc by a process wherein the substrate is polished with a pad while the abrasive composition is supplied between the substrate and the pad, and at least one of the pad and the substrate is rotated. The contents of the finely divided zirconium oxide particles, the abrasion promoter and the optional water-soluble oxidizing agent are 2–20 wt. %, 1–20 wt. % and up to 10 wt. %, respectively, based on the weight of the abrasive composition as used for polishing the substrate.

12 Claims, No Drawings

ABRASIVE COMPOSITION FOR MAGNETIC RECORDING DISC SUBSTRATE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an abrasive composition. More particularly, it relates to an abrasive composition used for polishing a substrate for a magnetic recording medium to give a magnetic recording disc having minimized surface irregularities, above which a magnetic head is capable of floating at a low flying height.

2. Description of the Related Art

Magnetic recording discs, i.e., memory hard discs, are widely used as memory means giving quick access to information as external memories of computers and word processors. The magnetic recording discs are made by a process wherein a substrate composed of an aluminum alloy disc blank with a nickel-phosphorus (NiP) surface coating, formed by electroless plating, is surface-polished, and then, a chromium underlayer, a cobalt alloy magnetic film and a carbon protective film are formed in this turn on the polished NiP surface by a sputter deposition.

If the substrate has irregularities on the polished surface which have a height larger than the flying height of a magnetic read/write head, when the magnetic head floating above the magnetic disc flies at a high speed, the head impinges upon the irregularities with the result of damage of the magnetic head. If the substrate for the magnetic recording disc has polish marks or irregularities, the marks or irregularities develop on the surfaces of the chromium underlayer, the cobalt alloy magnetic film and the carbon protective film in turn, and consequently a functional defect is caused on the magnetic recording disc. Thus it is necessary to polish the substrate surface with a high precision for giving a magnetic recording disc having a smooth surface.

A wide variety of abrasive compositions and polishing methods have heretofore been proposed for removing or minimizing irregularities on the surface of substrate for magnetic recording discs and providing a smooth substrate surface with neither polish marks nor irregularities. As examples of the proposed abrasive compositions or polishing methods, there can be mentioned (1) a two-stage polishing method using an abrasive composition comprising aluminum oxide having incorporated therewith (i) an oxidizing agent such as sodium hypochlorite, or colloidal aluminum, and (ii) cerium dioxide (Japanese Unexamined Patent Publication [hereinafter abbreviated to "JP-A"] 60-108489), (2) an abrasive composition comprising alumina having incorporated therein sulfamic acid or phosphoric acid (JP-A 61-291674), (3) an abrasive composition comprising alumina having incorporated therein aluminum nitrate (JP-A 62-25187), (4) an abrasive composition comprising alumina having incorporated therein boehmite (JP-A 1-188264), (5) an abrasive composition comprising alumina having incorporated therein a metal salt and boehmite (JP-A 1-205973), (6) an abrasive composition comprising alumina having incorporated therein a metal sulfite salt (JP-A 2-158682), (7) an abrasive composition comprising alumina having incorporated therein boehmite and an ammonium salt of an organic or inorganic acid (JP-A 2-158683), (8) a polishing method using an abrasive composition comprising an alumina slurry having pre-treated with an ultrasonic filter (JP-A 3-106984), (9) an abrasive composition comprising alumina having incorporated therein boehmite and a water-soluble peroxide (JP-A 3-115383), (10) an abrasive composition comprising alumina having incorporated therein an

amino acid (JP-A 4-108887), (11) an abrasive composition comprising alumina having incorporated therein (i) aluminum sulfate and/or aluminum chloride, and (ii) at least one compound selected from peroxide, nitric acid, a nitrate salt, a nitrite salt and an aromatic nitro compound (JP-A 4-275387), (12) an abrasive composition comprising alumina having incorporated therein a chelate compound, boehmite and an aluminum salt (JP-A 4-363385), (13) an abrasive composition comprising alumina having incorporated therein boehmite which has been obtained by heat-treating rectangular primary particles of gibbsite, and (14) an abrasive composition comprising colloidal silica particles and a chemical etching agent (JP-A 7-240025).

In the above-mentioned proposals (1) through (13), finely divided alumina or other aluminum compounds having an average particle diameter of about 1 μm are used as an abrasive, and thus, the substrate surfaces polished by these abrasive compositions exhibit a smoothness of an extent such that a practically acceptable flying height can be ensured. However, in these years, a lower flying height is eagerly desired for allowing recording density to be increased, and it is difficult or impossible by these proposals to provide a perfect substrate surface with a high precision on which the desired lower flying height can be achieved.

In the above-mentioned proposal (14), colloidal silica particles having an average particle diameter of several-tens nanometer are used as an adhesive, a polished substrate surface with a high precision can be obtained. However, the rate of polishing is low and thus the productivity is low, and, when polishing is conducted for a long time, the circumferential edge part of a substrate surface is undesirably abraded in excess.

When an abrasive with a high hardness is used for polishing, polish marks tend to occur on a substrate surface, and thus, an abrasive with an appropriate hardness should be chosen depending upon the particular hardness of the NiP coating on the substrate. Further, in view of the quality (such as absence of polish marks and reduced number of pits) required for an aluminum magnetic recording disc of the type above which a magnetic head floats at a low flying height, an abrasive having a particle diameter of submicrons and a sharp particle size distribution should be chosen.

In general an α -alumina is used as abrasive for an aluminum magnetic recording disc. However, α -alumina has a very high hardness as compared with that of the NiP coating, and therefore, when α -alumina is used as an abrasive for an aluminum disc of the type floating at a low flying height, the crystalline structure, the particle size distribution and other properties of the α -alumina abrasive should be strictly controlled. Further, finely divided alumina particles have a problem such that, although grinding or pulverizing is employed for the industrial production thereof, the yield of particles of the desired size is low and thus their productivity is low.

In contrast to α -alumina abrasive, a silica abrasive has a low hardness and does not cause polish marks and pits on the substrate surface. However, the rate of polishing is very low and the productivity is low.

SUMMARY OF THE INVENTION

A primary object of the present invention is to provide an abrasive composition used for polishing a substrate for a magnetic recording disc at a high rate to give a magnetic recording disc having a reduced surface roughness, minimized surface irregularities and polish marks, and exhibiting a high recording density.

If a water-soluble oxidizing agent is further incorporated in the abrasive composition, the abrading action is more enhanced. As specific examples of the water-soluble oxidizing agent, there can be mentioned hydrogen peroxide (H_2O_2), nitric acid, potassium permanganate ($KMnO_4$), perchloric acid ($HClO_4$), sodium perchlorate ($NaClO_4$) and sodium hypochlorite ($NaClO$).

Auxiliary ingredients can be incorporated in the aqueous abrasive composition comprising the finely divided zirconium oxide particles, the abrasion promoter, water and the optional water-soluble oxidizing agent. The auxiliary ingredients include, for example, a surface active agent, a preservative and a PH adjuster such as an alkali or an acid. For example, when the abrasive composition contains an acid salt of aluminum such as aluminum nitrate as an abrasion promoter, pH of the abrasive composition is preferably adjusted to a value of 2 to 5.

The contents of the above-mentioned ingredients in the aqueous abrasive composition of the present invention as used for polishing a substrate for a magnetic recording disc are as follows. It is convenient that, when the aqueous abrasive composition is as-made and in storage, the contents of the respective ingredients are high (i.e., the abrasive composition is concentrated), and, when it is applied for polishing the substrate, the abrasive composition is diluted to the desired concentration, explained below.

The content of finely divided zirconium oxide particles is preferably 2 to 20% by weight based on the weight of the abrasive composition. If the content of zirconium oxide is lower than 2% by weight, the rate of polishing is lowered and a long time is required for completion of polishing. Even if the content of zirconium oxide is higher than 20% by weight, the rate of polishing is not enhanced and the abrasive composition is not economical.

The content of the abrasion promoter is preferably in the range of 1 to 20% by weight, more preferably 2 to 15% by weight, based on the weight of the abrasive composition. When the content of the abrasion promoter is too low, the rate of polishing is lowered, a long time is required for completion of polishing, and the circumferential edge part of the substrate surface is undesirably abraded in excess. As the content of the abrasion promoter is increased, the rate of polishing increases until the content reaches about 15% by weight, but, when the content exceeds about 15% by weight, it increases only to a negligible extent. Any baneful influence is not exerted on the polished surface when the content exceeds about 15% by weight, but, the upper limit is 20% by weight from an economical viewpoint.

The content of the optional water-soluble oxidizing agent is preferably not larger than 10% by weight based on the weight of the abrasive composition, for enhancement of the abrading action. Even if the content of the oxidizing agent exceeds 10% by weight, the enhancement of abrading action is rather reduced.

The substrate for a magnetic recording disc to be polished with the aqueous abrasive composition of the present invention is not particularly limited. However, the abrasive composition of the present invention is advantageously used for polishing substrates made of a disc blank of aluminum or an aluminum alloy such as an aluminum-magnesium alloy. As preferable examples of the substrates, there can be mentioned aluminum or aluminum alloy disc blanks, which have been plated with nickel-phosphorus (NiP), nickel-copper (NiCu) or cobalt-phosphorus (CoP), or which have been subjected to anodic oxidation.

The polishing of the substrate can be effected by a process wherein the substrate is polished with a pad while the

aqueous abrasive composition of the present invention is supplied between the substrate and the pad, and at least one of the pad and the substrate is rotated.

The substrate polished with the abrasive composition of the present invention have extremely minimized surface irregularities. The surface roughness (Ra) is about 3 to 5 angstroms and thus the smoothness is excellent.

The invention will now be described by the following examples wherein % is by weight unless otherwise specified.

Characteristics of polished substrates and magnetic recording discs were evaluated by the following methods.

(1) Rate of abrasion

After completion of polishing, a polished substrate was washed with water, dried and then the weight reduction due to polishing was measured. The reduction of thickness (μm) of the substrate was calculated from the weight reduction, and the rate of abrasion was expressed by the reduction of substrate thickness (μm) per minute.

(2) Surface roughness (Ra) of substrate

The surface roughness (Ra) of a polished substrate was measured by a Talystep and a Talydata 2000 (supplied by Rank Taylor Hobson Co.).

(3) Polish marks and pits on substrate

The presence of polish marks on a polished substrate was observed by the naked eye under irradiation with a halogen lamp in a dark room.

The surface defect on the polished substrate was observed by a differential interference contrast microscope with 50X magnification, and the results were expressed by the number of pits per substrate surface.

(4) Missing-pulse errors

A magnetic recording disc was tested by a glide certifier tester RQ-3000, supplied by Hitachi DECO Co., under the following testing conditions.

Track width: 3 μm

Recording density: flux variation 70,000 per inch

Flying height of head: 2.0 micro-inch (50.8 nm)

Number of revolution: 4,500 rpm

Slice level: 65%

Missing-pulses smaller than a slice level of 65%, i.e., missing-pulses wherein the ratio of the output waveform to the input waveform was smaller than 65%, were rated as missing-pulse errors. The evaluation results were expressed by the number of missing-pulse errors per disc.

(5) Flying height (μm) of magnetic head

By using the above-mentioned glide certifier tester, a head was allowed to float above the magnetic disc, and, while the flying height of the magnetic head was gradually reduced, the lowest permissible flying height was measured at which the head commenced to impinge on irregularities on the disc surface.

EXAMPLES 1-16 AND COMPARATIVE EXAMPLES 1, 2

Preparation of Abrasives

Finely divided zirconium oxide particle abrasives used in Examples 1-16 were prepared as follows.

In a two-liter beaker, 250 g of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$), 260 ml of pure water and 320 ml of 2.8 N aqueous ammonia were mixed together, and the obtained solution was put in a one-liter glass autoclave. The solution

The evaluation results of polishing rate of the substrate, surface roughness of the polished substrate, and presence of polish marks and number of pits on the polished substrate, number of missing-pulse errors on the magnetic recording disc, and flying height of a magnetic head are shown in Table 2.

TABLE 2

	Polishing rate ($\mu\text{m}/\text{min}$)	Surface roughness R_a (angstrom)	Polish marks	Surface flaw (pits/ disc)	Flying height of head (μm)	Missing- pulse errors (/disc)
Ex. 1	0.19	4	No	0	0.017	0
Ex. 2	0.33	3	No	0	0.016	0
Ex. 3	0.36	5	No	0	0.017	0
Ex. 4	0.38	4	No	0	0.017	0
Ex. 5	0.21	5	No	3	0.017	0
Ex. 6	0.24	3	No	0	0.017	0
Ex. 7	0.30	4	No	0	0.016	0
Ex. 8	0.34	3	No	0	0.016	0
Ex. 9	0.35	4	No	0	0.017	0
Ex. 10	0.31	4	No	0	0.016	0
Ex. 11	0.16	5	No	0	0.016	0
Ex. 12	0.20	4	No	0	0.017	0
Ex. 13	0.24	5	No	0	0.017	0
Ex. 14	0.16	5	No	0	0.016	0
Ex. 15	0.20	4	No	0	0.016	0
Ex. 16	0.19	4	No	0	0.016	0
C.E. 1	0.60	15	Found	40	0.022	>60
C.E. 2	0.12	2	No	0	0.015	0

Note.

C.E. Comparative Example

As seen from Table 1 and Table 2, when alumina is used as an abrasive (Comparative Example 1), the rate of polishing is high, but the polished substrate surface has large surface roughness, polish marks and many bits, and the magnetic recording disc exhibits high flying height of magnetic head and many missing-pulse errors. When colloidal silica is used as an abrasive (Comparative Example 2), the rate of polishing is low although other characteristics are satisfactory.

In contrast, when the abrasive composition containing zirconium oxide of the present invention is used (Examples 1-16), the rate of polishing is high, occurrence of polish marks and bits on the polished surface is not found or found only to a negligible extent, and there is no occurrence of missing-pulse error on the magnetic recording disc. Further the flying height of head above the magnetic recording disc is low, namely, irregularities on the disc are minimized. Therefore, the magnetic recording disc made by using the abrasive composition of the present invention is suitable for magnetic recording at a high recording density employing an MR head.

What is claimed is:

1. An abrasive composition for polishing a substrate for a magnetic recording disc, which comprises, based on the weight of the abrasive composition used for polishing the substrate, 2 to 20% by weight of finely divided zirconium oxide particles, 1 to 20% by weight of an abrasion promoter and water.

2. The abrasive composition according to claim 1 wherein the finely divided zirconium oxide particles have a size such that primary particles thereof have an average particle diameter in the range of 0.001 to 0.3 μm and secondary particles thereof have an average particle diameter of 0.1 to 1.0 μm .

3. The abrasive composition according to claim 1 wherein the finely divided zirconium oxide particles have a particle size distribution such that the diameter (D_{90}) at a cumulative distribution of 90% by weight in particle size distribution of secondary particles thereof and the diameter (D_{10}) at a cumulative distribution of 10% by weight in particle size distribution of secondary particles thereof satisfy the requirement that the ratio of D_{90}/D_{10} is 3.0 or less.

4. The abrasive composition according to claim 1 wherein the abrasion promoter is an aluminum salt of an acid.

5. The abrasive composition according to claim 4 wherein the aluminum salt is aluminum nitrate.

6. The abrasive composition according to claim 1 which further comprises not more than 10% by weight or less, based on the weight of the abrasive composition used for polishing the substrate, of a water-soluble oxidizing agent.

7. The abrasive composition according to claim 6 wherein the water-soluble oxidizing agent is selected from the group consisting of hydrogen peroxide, nitric acid, potassium permanganate, perchloric acid, sodium perchlorate and sodium hypochlorite.

8. An improvement in a process for polishing a substrate for a magnetic recording disc wherein the substrate is polished with a pad while an abrasive composition is supplied between the substrate and the pad, and at least one of the pad and the substrate is rotated, the process comprising using an abrasive composition comprising, based on the weight of the abrasive composition used for polishing the substrate, 2 to 20% by weight of finely divided zirconium oxide particles, 1 to 20% by weight of an abrasion promoter and water.

9. The process according to claim 8 wherein the finely divided zirconium oxide particles have a size such that primary particles thereof have an average particle diameter in the range of 0.001 to 0.3 μm and secondary particles thereof have an average particle diameter of 0.1 to 1.0 μm .

10. The process according to claim 8 wherein the abrasion promoter is an aluminum salt of an acid.

11. The process according to claim 8 wherein the abrasive composition further comprises not more than 10% by weight, based on the weight of the abrasive composition as used for polishing the substrate, of a water-soluble oxidizing agent.

12. The process according to claim 8 wherein the substrate for a magnetic recording disc is a disc blank made of aluminum or an aluminum alloy, which has been plated with nickel-phosphorus, nickel-copper or cobalt-phosphorus, or which has been subjected to anodic oxidation.

* * * * *

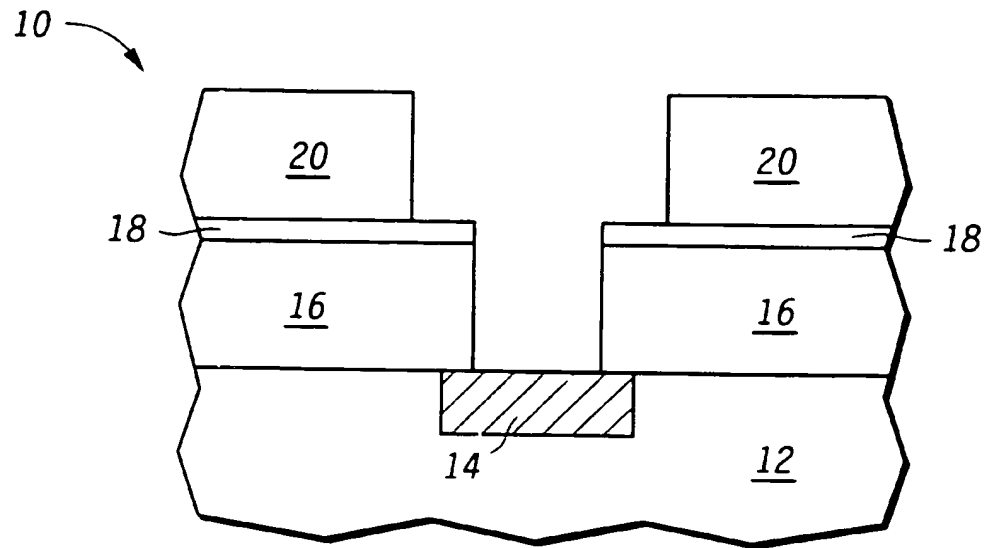


FIG. 1

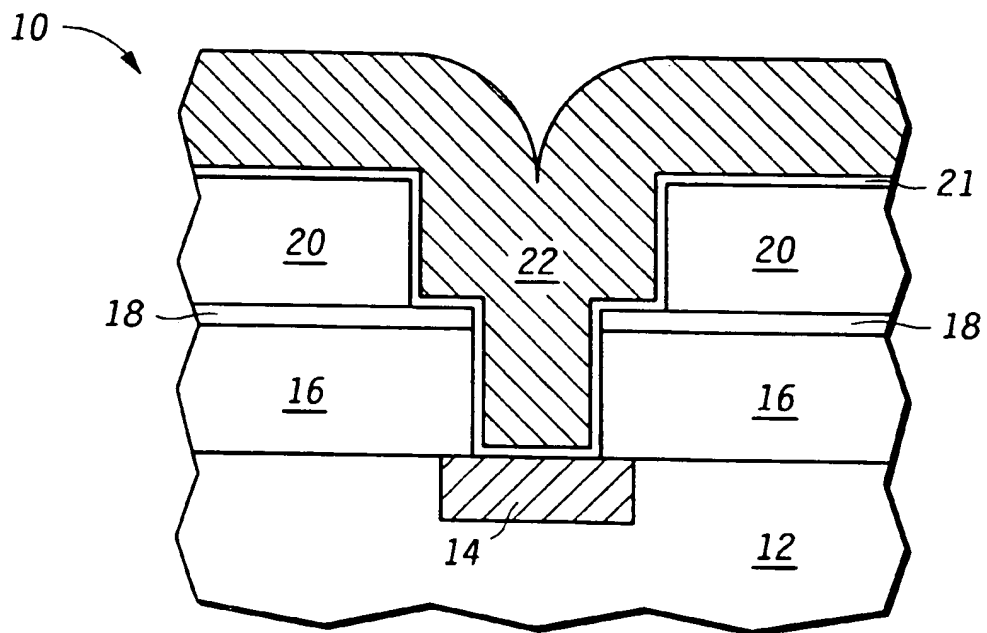


FIG. 2

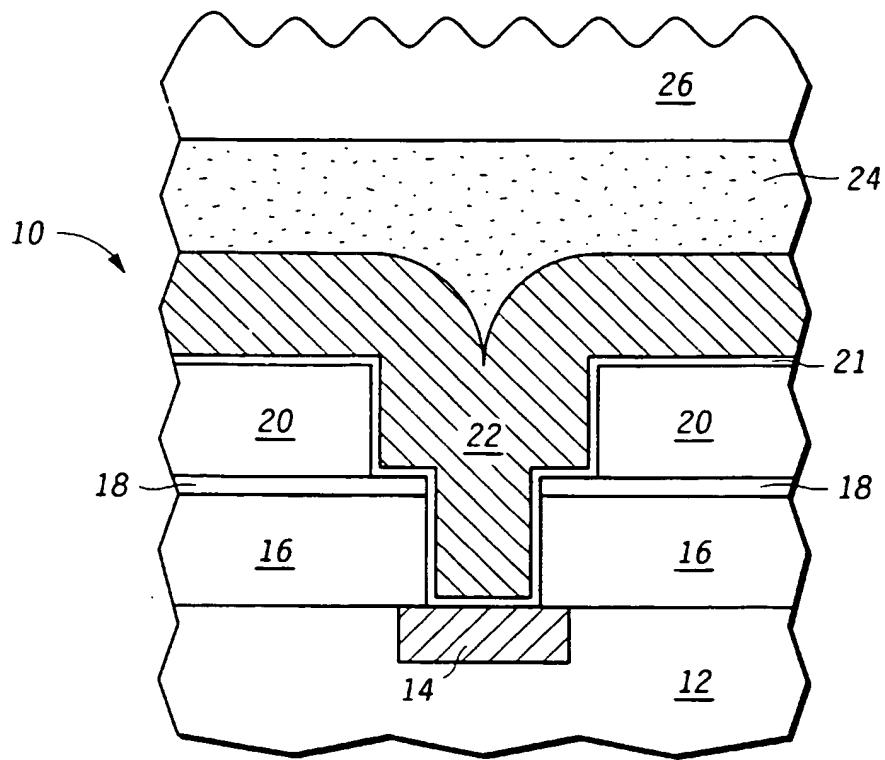


FIG. 3

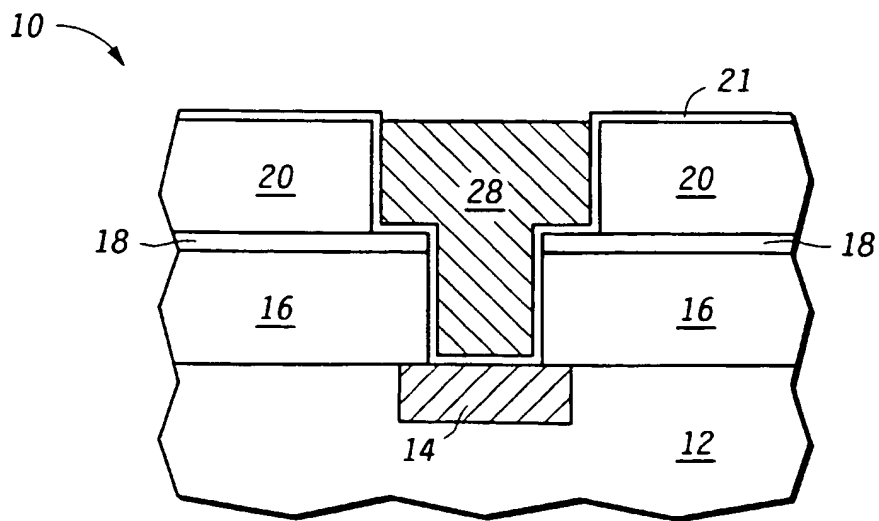


FIG. 4

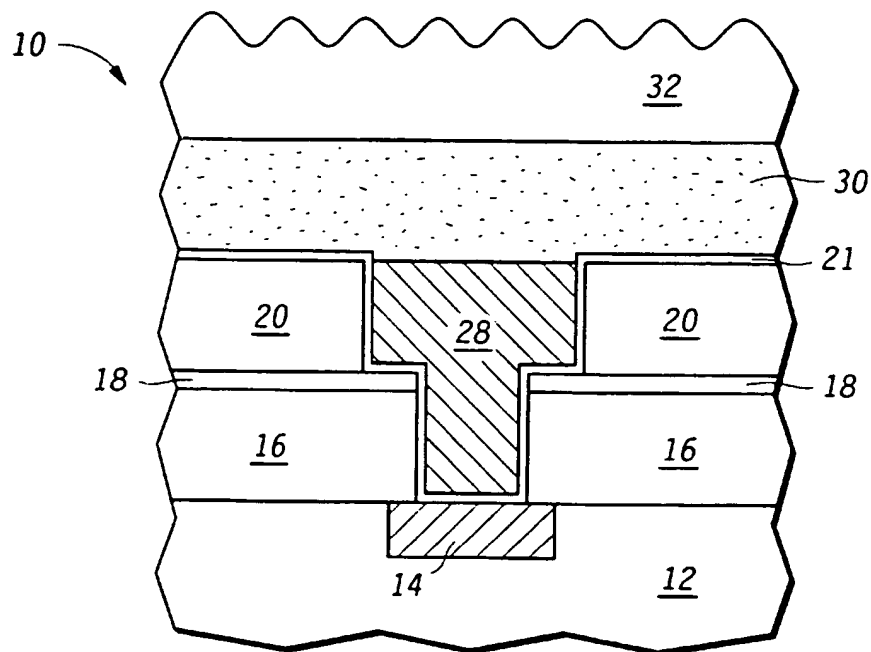


FIG. 5

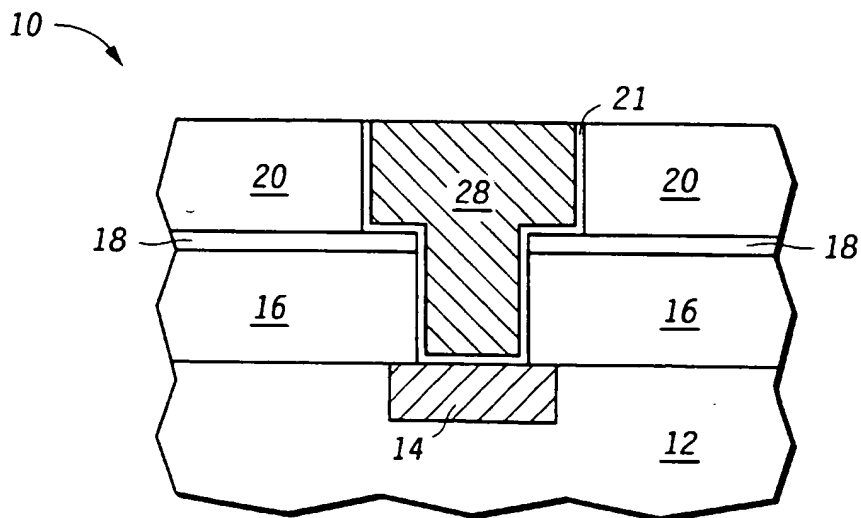


FIG. 6

CHEMICAL MECHANICAL POLISHING (CMP) SLURRY FOR POLISHING COPPER INTERCONNECTS WHICH USE TANTALUM- BASED BARRIER LAYERS

FIELD OF THE INVENTION

The present invention relates generally to semiconductor manufacturing, and more particularly to, a two-step CMP process for copper interconnects which utilize Ta-based alloys as barrier layers in integrated circuits (ICs).

BACKGROUND OF THE INVENTION

The integrated circuit (IC) industry is currently researching and developing new metallic interconnect materials and structures which can be used within integrated circuits (ICs). A promising metallic material which will be used in the future for integrated circuit (IC) interconnects is copper (Cu). Copper is desired in the integrated circuit industry since copper has improved electromigration resistance over aluminum and other metallic materials which are currently being used in the integrated circuit industry. In addition, copper has a lower resistivity than other commonly used metallic materials, whereby the performance of integrated circuit devices can be greatly improved through the use of copper interconnects. Also, copper interconnects allow an integrated circuit to use higher critical current.

However, there is currently no known technology which can effectively plasma etch or wet etch copper materials so that functional copper interconnects are adequately formed over the surface of an integrated circuit. In order to overcome this limitation, copper chemical mechanical polishing (CMP) has been suggested as the most promising alternative which can render proper formation of copper interconnects on an integrated circuit. Therefore, the industry is currently searching for an optimal chemical mechanical polishing (CMP) slurry which can be used to form copper interconnects on an integrated circuit (IC).

In addition, copper readily diffuses into conventional silicon-based materials such as polysilicon, single-crystalline silicon, silicon dioxide, low-k inorganic and organic materials, and the like. Once these silicon-based materials have been contaminated with Cu atoms, the dielectric constant of the silicon-based dielectrics is adversely affected. In addition, once semiconductive silicon-based materials are Cu doped, transistors made within or in close proximity to the Cu doped silicon-based regions either cease to function properly or are significantly degraded in electrical performance. Therefore, in addition to the challenges of finding an adequate copper polishing process, an adequate copper barrier material is also needed. In addition, this barrier material must be integrated with the CMP process to obtain optimal electrical performance, optimal planarization, improved throughput, etc., in order to render copper technology in IC designs feasible.

It is known to use one of $\text{Fe}(\text{NO}_3)_3$, HNO_3 , HN_4OH , or KMnO_4 to perform polishing of copper. These chemical compounds have been extensively researched by CMP engineers in an attempt to discover an optimal copper CMP process. However, the use of these known chemicals has not yet produced optimal copper polishing results. For example, various experimentation performed using the known chemistries described above have resulted in one or more of: (1) poor removal rate whereby CMP throughput is inadequate; (2) excessive pitting and/or corrosion of the copper material whereby device performance and device yield is reduced; (3) layer planarity problems; (4) poor IC electrical perfor-

mance; or (5) poor selectivity to copper over adjacent oxide materials ("oxide" refers to "silicon dioxide" and the two may be used interchangeably herein.). In addition, the current CMP research using copper interconnects with tantalum-based barriers has shown that most widely-used copper CMP processes have high selectivity to tantalum-based alloys. With the high copper to tantalum selectivity of current copper polishing, a wafer must either be: (1) significantly overpolished to ensure adequate tantalum-based barrier material removal whereby copper regions are significantly dished (i.e., poor planarity results); or (2) polished less aggressively whereby some tantalum-based barrier material may remain on the device causing short circuits or excessive leakage paths in the IC.

Therefore, a need exist in the industry for an improved CMP slurry which may be used to manufacture copper interconnects while reducing or eliminating one or more of the above common copper CMP problems when copper is used in conjunction with a tantalum-based material. This improved slurry should have one or more of: good removal rate whereby CMP throughput is improved; reduced or eliminated pitting and corrosion of the copper material whereby device performance and yield is improved; improved planarity of the copper layer; improved electrical performance of integrated circuits, adequate selectivity of copper to oxide; and improved removal of a tantalum-based barrier without adversely affecting the overall copper structure.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1-6 illustrate, in cross-sectional diagrams, a method for forming a chemical mechanical polish (CMP) copper interconnect which uses a tantalum-based barrier layer whereby polishing occurs in accordance with the present invention.

It will be appreciated that for simplicity and clarity of illustration, elements illustrated in the drawings have not necessarily been drawn to scale. For example, the dimensions of some of the elements are exaggerated relative to other elements for clarity. Further, where considered appropriate, reference numerals have been repeated among the drawings to indicate corresponding or analogous elements.

DESCRIPTION OF A PREFERRED EMBODIMENT

Generally, the present invention is a two-step chemical mechanical polishing (CMP) process for forming a copper interconnect on an integrated circuit (IC) wherein the copper interconnect uses a tantalum-based barrier layer. This two step CMP process uses a novel slurry taught herein which improves copper interconnect technology. The copper interconnect polish step taught herein uses a novel copper-polishing slurry and a hard polishing pad to polish a bulk of the copper material to expose top portions of the barrier layer. The copper polish process stops reasonably well on the tantalum-based barrier layer whereby overpolishing of the copper (Cu or copper alloy) is avoided. After removing a bulk of the copper material, a second slurry and a softer polishing pad are used to polish away upper portions of the tantalum-based barrier layer reasonably selective to the oxide and the copper. This second polishing step in the two-set polishing process may take the place of an oxide touch-up polish process which is typically used after conventional copper polishing.

It has been experimentally shown that the use of this two step copper interconnect CMP process, whereby a first

set of atoms) or a copper alloy (which is intentionally doped with another atom other than Cu). In addition, this CVD copper layer may also chemically interact with the previously deposited barrier layer 21 to form at least an interface/ bottom alloy material comprising both tantalum and copper. The CVD copper layer may be replaced with an ionized metal plasma (IMP) layer of copper or an IMP layer of a copper alloy. Also, collimated physical vapor deposition or electroless copper processing may be used for form the seed layer. Typically, the copper material which is deposited in FIG. 1 has a copper concentration of greater than 80%. A thin seed layer other than copper may be used in some embodiments.

After formation of the IMP and/or CVD copper layer, an electroplating process is used to form additional copper material on top of the CVD or IMP copper seed layer to form the entire thickness of layer 22. Typically, copper electroplating is performed until an overall thickness of the layer 22 of roughly 7,000–15,000 Å is achieved. In the alternative copper CVD or copper PVD may be used to complete the thickness of the copper layer in FIG. 2. The electroplated copper may either be pure copper or a copper composite material as discussed hereinabove.

FIG. 3 illustrates that the structure 10 of FIG. 1 is placed into a chemical mechanical processing (CMP) tool. The CMP tool of FIG. 3 preferably has two platens wherein one platen is a hard platen (i.e., a harder polishing pad) and the other polishing platen is a soft polishing platen (i.e., a softer polishing pad than the hard polishing pad). In another form, two different polishing tools may be used (one with a harder pad and another with a softer pad) or the same polishing tool may be used whereby the tool has platens which are easily interchanged to enable quick changes in pad hardness with little down time.

The copper layer 22 of FIG. 1 is placed into contact with a chemical mechanical polishing (CMP) slurry 24 as illustrated in FIG. 3. The harder chemical mechanical polishing pad 26 in the CMP tool is placed in contact with the slurry 24 and is mechanically rotated and applied with pressure in order to result in effective chemical/mechanical removal of upper portions of the layer 22 in FIG. 3.

In order to remove copper material from layer 22, the slurry 24 forms a thin (e.g., tens of angstroms) copper oxide or oxidized layer on a top surface of the layer 22. This thin oxidized copper layer is formed due to the exposure of the layer 22 to the slurry 24 in FIG. 2. In essence, the slurry 24 contains an oxidizing species which oxidizes a thin top portion of the layer 22 to form the thin copper oxide layer on a top of the layer 22. Other chemical species within the slurry 24 will chemically attack this oxidized layer to dissolve the copper oxide layer into the slurry 24. In addition, various particles or abrasive slurry materials within the slurry 24 along with the mechanical movement of the polishing pad 26 results in mechanical abrasion of the oxidized layer to further effectuate removal of the layer 22 over time. Through progressive oxidation and removal of oxidized copper, top surfaces of the layer 22 are incrementally removed to enable effective copper chemical mechanical polishing (CMP).

The slurry 24, illustrated in FIG. 3, contains an oxidizing agent, a carboxylate salt (e.g., a citrate salt), an abrasive slurry/agent, a solvent, and an optional triazole or triazole derivative. Specifically, the oxidizing agent which can be utilized within the slurry is hydrogen peroxide (H_2O_2). Carboxylate salts which have been shown to be effective for removal of copper includes one of many citrate salts such as

one or more of ammonium citrate or potassium citrate. A typical abrasive which has been experimentally shown to result in good copper removal and planarization is an alumina abrasive, but a silica abrasive in lieu of the alumina abrasive or in addition with the alumina abrasive may be advantageous. In addition, an optional triazole derivative or triazole solution may be added to the slurry. It was experimentally found, for example, that the addition of 1,2,4-triazole to the copper CMP slurry has been shown to improve copper planarization by reducing the amount of copper recessing into oxide trench openings. Typical solvents used in the slurry 24 of FIG. 2 is one or more of deionized water (H_2O) or an alcohol.

In general, the oxidizing agent (H_2O_2) of the slurry 24 may be within any range of roughly 0.2 weight percent (wt %) to 5.0 weight percent (wt %). The carboxylate salt or citrate salt can be within a range of roughly 0.2 weight percent to roughly 20 weight percent. The abrasive slurry/agent (alumina abrasive) is roughly 1.0 weight percent to 12.0 weight percent of the slurry 24. In addition, an optional triazole or triazole derivative can be provided within the slurry 24 to be roughly 0.05 weight percent to 2.0 weight percent of the slurry 24. A remaining balance of the slurry 24 is typically deionized water and/or an alcohol solution.

In a preferred form, it has been experimentally shown that adequate copper (Cu) polishing has been achieved using a hydrogen peroxide range between 1.0 weight and 1.5 weight percent, a citrate salt concentration within the range of 0.8 weight percent and 1.3 weight percent, an alumina abrasive concentration within the range of 2.0 weight percent and 4.0 weight percent, a triazole concentration between roughly 0.1 weight percent and 0.2 weight percent, and a remaining balance solvent. A preferred solution within this range which has been utilized is 1.2 weight percent hydrogen peroxide, 1.1 weight percent ammonium citrate, 3.0 weight percent alumina slurry, 0.12 weight percent, 1,2,4-triazole, and a remaining balance deionized water (H_2O).

In this preferred form, the copper polishes at or above roughly a 4000 angstroms/min rate or more. TaSiN barrier materials polish at a rate of 350 angstroms/min or less, and silicon dioxide polishes at a rate of 250 angstroms/min or less. Slower polishing times are possible, but will affect throughput. Therefore, the Cu polishing process of FIG. 3 will effectively stop on the tantalum-based barrier layer 21 as shown in FIG. 4.

FIG. 4 illustrates that the first step of the two-step chemical mechanical polishing (CMP) process is complete. The first step used the slurry 24 and harder platen/pad 26 to polish copper material until a copper interconnect 28 is formed as illustrated in FIG. 4. The copper interconnect is formed when all copper material is removed from all areas outside the trench opening in layer 20 and the via opening in layer 16. In a preferred form, the interconnect 28 would be formed co-planar with the top surface of the layer 21. However, some recessing/dishing of the copper layer 22 can occur in most CMP systems resulting in a slight recess of the copper portion of the interconnect 28 as shown in FIG. 4. It should be noted that this recess/dishing can be compensated for by the subsequent removal of the tantalum-based barrier by the second CMP polishing step. In other words, the second polish step may reduce the effects of dishing/recess. It is important to note that the presence of the triazole or triazole derivative in the CMP slurry has been experimentally shown to also reduce this adverse recessing of the copper interconnect 28. In addition, the presence of the TaSiN (which is subsequently removed and acts as a copper polish stop) ensures that the overall recess of the copper

8. The method of claim 7 wherein citrate salt is ammonium citrate.

9. The method of claim 1 wherein the second CMP slurry comprises:

on an order of 1.0 wt % to 12.0 wt % of an abrasive slurry; and

on an order of 0.01 wt % to 2.0 wt % of an amine compound.

10. The method of claim 9 wherein abrasive slurry is a silica abrasive.

11. The method of claim 9 wherein the second CMP slurry has a pH between 9 and 11.

12. The method of claim 1 wherein the first CMP slurry polishes the copper layer at a rate of greater than 5000 angstroms per minute and polishes the tantalum-based barrier layer at a rate of less than 350 angstroms per minute, and wherein the second CMP slurry polishes the copper layer at a rate of less than 400 angstroms per minute and polishes the tantalum-based barrier layer at a rate of greater than 450 angstroms per minute.

13. The method of claim 1 wherein the first CMP slurry is used in conjunction with a first polishing pad and the second CMP slurry is used in conjunction with a second polishing pad wherein the second polishing pad is softer than the first polishing pad.

14. The method of claim 1 wherein the step of forming the dielectric layer comprises:

forming the dielectric layer from several dielectric layers and at least one etch stop layer whereby the opening in the dielectric layer is formed as a dual inlaid opening.

15. The method of claim 1 wherein the tantalum-based barrier layer comprises one of either tantalum nitride or tantalum silicon nitride.

16. A method of polishing a copper layer having a tantalum-based barrier layer, the method comprising the steps of:

providing a dielectric layer;

forming an opening in the dielectric layer;

forming the tantalum-based barrier layer within the opening;

forming the copper layer over the tantalum-based barrier layer;

polishing the copper layer using a first CMP process comprising a carboxylate salt; and

polishing the tantalum-based barrier layer using a second CMP process comprising an amine compound.

17. The method of claim 16 wherein the first CMP process uses a first CMP pad and the second CMP process uses a second CMP pad wherein the first CMP pad is harder than the second CMP pad.

18. The method of claim 16 wherein the first CMP process uses a first CMP slurry and the second CMP process uses a second CMP slurry wherein the first CMP slurry is different from the second CMP slurry.

19. The method of claim 18 wherein the first CMP slurry comprises:

on an order of 0.2 wt % to 5 wt % of an oxidizing agent;

on an order of 0.2 wt % to 20 wt % of a carboxylate salt; and

on an order of 1.0 wt % to 12 wt % abrasive slurry; and the second CMP slurry comprises:

on an order of 1.0 wt % to 12.0 wt % of an abrasive slurry; and

on an order of 0.01 wt % to 2.0 wt % of an amine compound.

20. The method of claim 18 wherein the first CMP slurry comprises an alumina abrasive slurry and the second CMP slurry comprises a silica abrasive slurry.

21. The method of claim 18 wherein the first CMP slurry comprises an alumina abrasive slurry and the second CMP slurry comprises a silica abrasive slurry.

22. The method of claim 18 wherein the first CMP slurry comprises an oxidizing agent and the second CMP slurry does not contain an oxidizing agent.

23. The method of claim 18 wherein the first CMP slurry polishes the copper layer at a rate of greater than 5000 angstroms per minute and polishes the tantalum-based barrier layer at a rate of less than 350 angstroms per minute, and wherein the second CMP slurry polishes the copper layer at a rate of less than 400 angstroms per minute and polishes the tantalum-based barrier layer at a rate of greater than 450 angstroms per minute.

24. The method of claim 18 wherein the second CMP slurry comprises ethylenediamine.

25. The method of claim 16 wherein the tantalum-based barrier layer comprises one of either tantalum nitride or tantalum silicon nitride.

26. A method for forming a copper layer having a tantalum-based barrier layer, the method comprising the steps of:

forming a first dielectric layer;

forming a second dielectric layer over the first dielectric layer, the second dielectric layer having a top surface;

etching an interconnect trench in the second dielectric layer;

etching a via opening in the first dielectric layer;

depositing the tantalum-based barrier layer within the interconnect trench and the via opening;

depositing the copper layer on top of the tantalum-based barrier layer;

polishing, using a first CMP process, the copper layer to expose a portion of the tantalum-based barrier layer, the first CMP process polishing the copper layer faster than the tantalum-based barrier layer; and

polishing, using a second CMP process different from the first CMP process, the tantalum-based barrier layer to expose the top surface of the second dielectric layer, the second CMP process polishing the tantalum-based barrier layer faster than the copper layer and polishing the tantalum-based barrier layer faster than the second dielectric layer wherein the first CMP slurry is used in conjunction with a first polishing pad and the second CMP slurry is used in conjunction with a second polishing pad wherein the second polishing pad is softer than the first polishing pad.

27. The method of claim 26 wherein the first CMP process uses a slurry comprising:

on an order of 0.2 wt % to 5 wt % of hydrogen peroxide;

on an order of 0.2 wt % to 20 wt % of an ammonium citrate; and

on an order of 1.0 wt % to 12 wt % alumina slurry; and the second CMP process uses a slurry comprising:

on an order of 1.0 wt % to 12.0 wt % of a silica slurry; and

on an order of 0.01 wt % to 2.0 wt % of ethylenediamine.

28. The method of claim 27 wherein the second CMP process uses a slurry that has a non-neutral basic pH.

29. The method of claim 28 wherein the second CMP process uses a slurry that has a non-neutral basic pH within a range of 9.0 and 11.0.

United States Patent [19]
Rostoker et al.

US005389194A
[11] Patent Number: **5,389,194**
[45] Date of Patent: **Feb. 14, 1995**

[54] **METHODS OF CLEANING
SEMICONDUCTOR SUBSTRATES AFTER
POLISHING**

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Calif.**

[73] Assignee: **LSI Logic Corporation, Milpitas,
Calif.**

[21] Appl. No.: **77,809**

[22] Filed: **Jun. 15, 1993**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 14,432, Feb. 5, 1993,
abandoned.

[51] Int. Cl.⁶ **H01L 21/306**

[52] U.S. Cl. **156/636; 437/228;
437/946; 252/79.3**

[58] Field of Search **252/79.3; 156/636;
437/228, 946; 51/281 R, 283 R**

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Primary Examiner—Brian E. Hearn

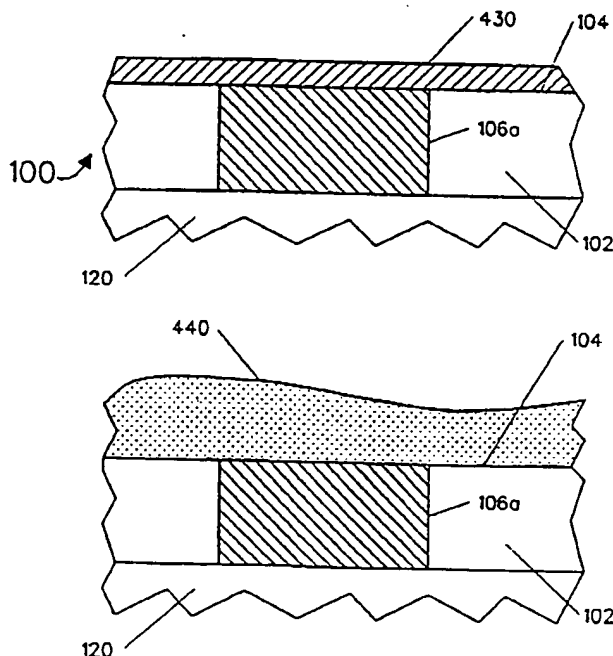
Assistant Examiner—Trung Dang

Attorney, Agent, or Firm—Honigman Miller Schwartz
and Cohn

[57] **ABSTRACT**

A method of cleaning semiconductor substrates after polishing, particularly chem-mech polishing a semiconductor substrate to planarize a layer, to remove excess material from atop a layer, and to strip back a defective layer is disclosed. Aluminum oxide particles having a small, well controlled size, and substantially in the alpha phase provide beneficial results when polishing. A phosphoric acid cleaning solution is used. The aluminum oxide particles are soluble in the phosphoric acid solution, which does not significantly attack silicon dioxide. The phosphoric acid solution can include a small concentration of hydrofluoric acid to aid in removing silicon dioxide detritus from the surface of the wafer.

25 Claims, 4 Drawing Sheets



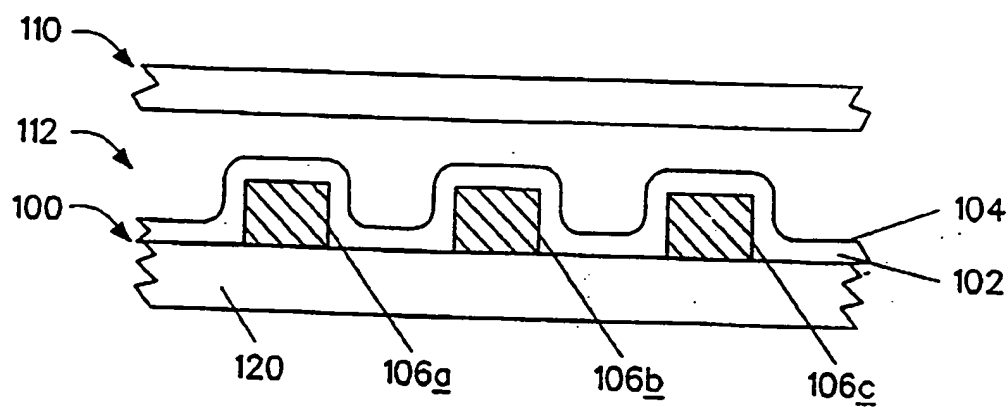


FIG. 1a

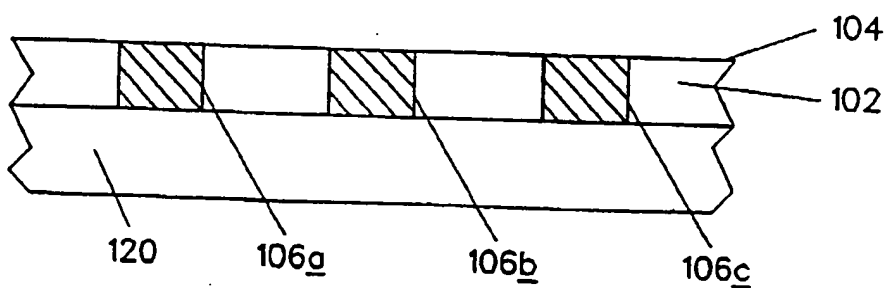


FIG. 1b

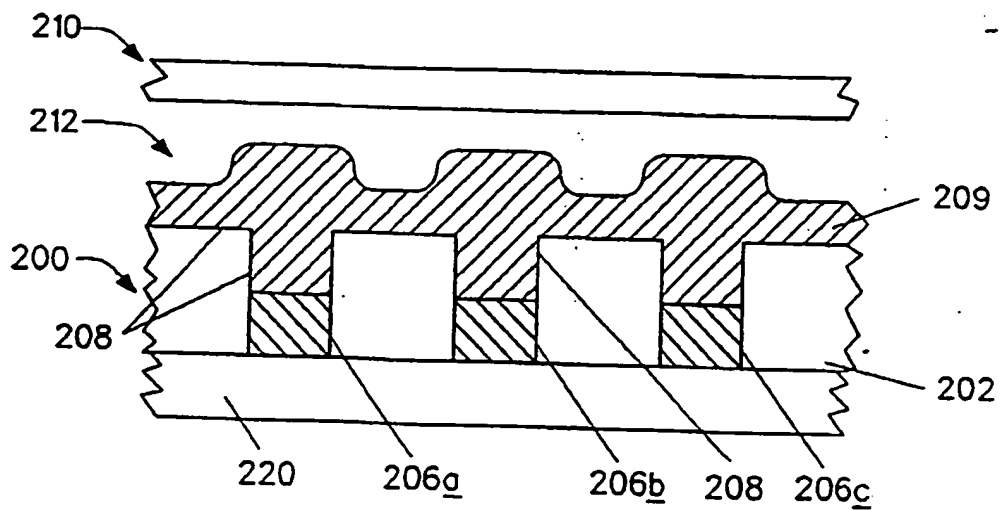


FIG. 2a

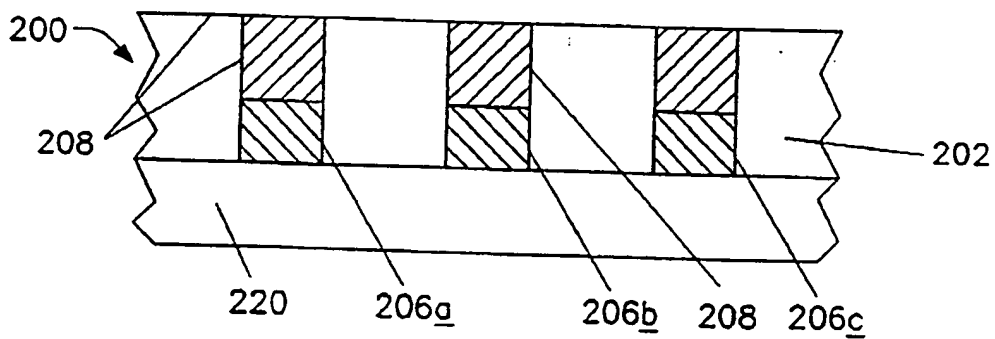


FIG. 2b

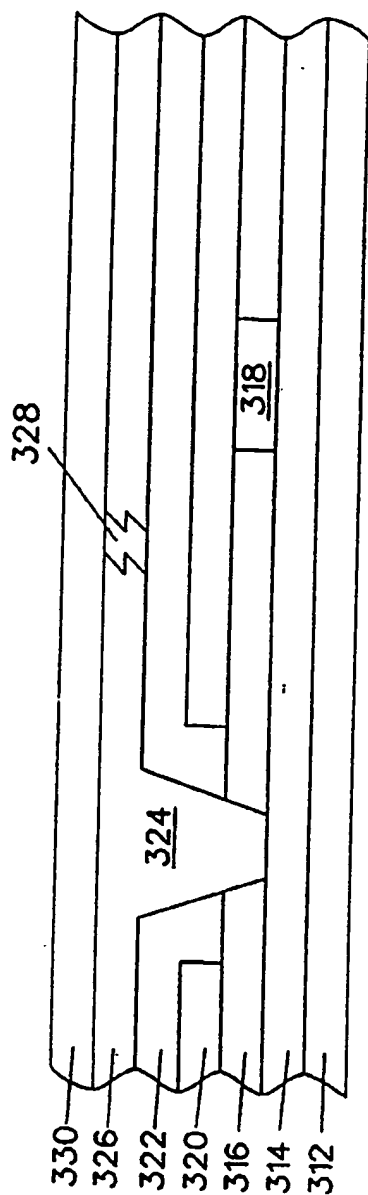


FIG. 3

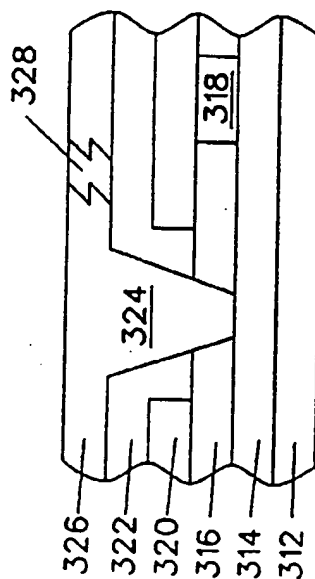


FIG. 3a

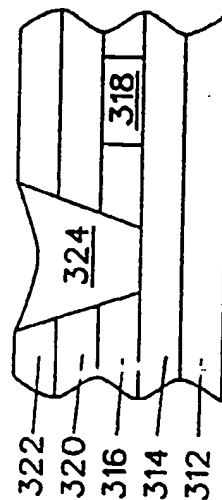


FIG. 3b

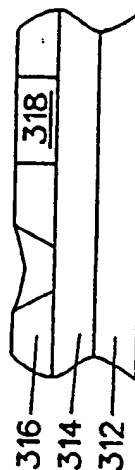


FIG. 3c

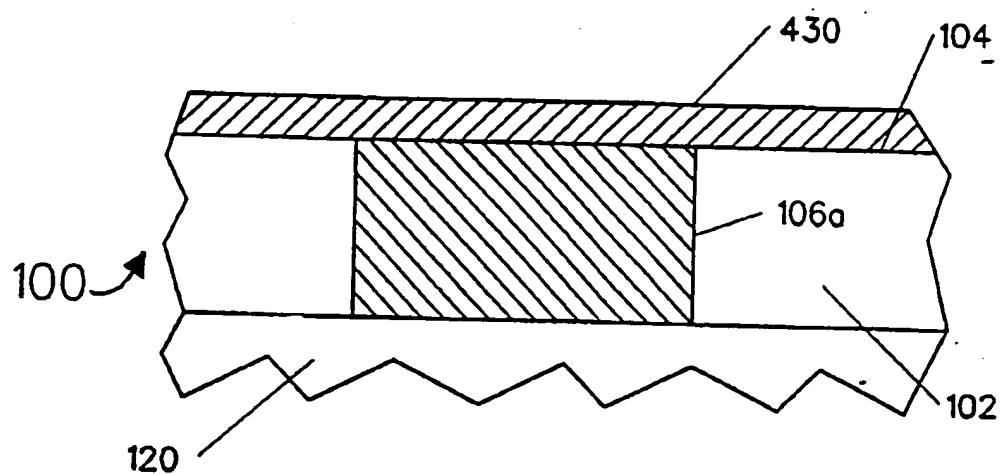


FIG. 4a

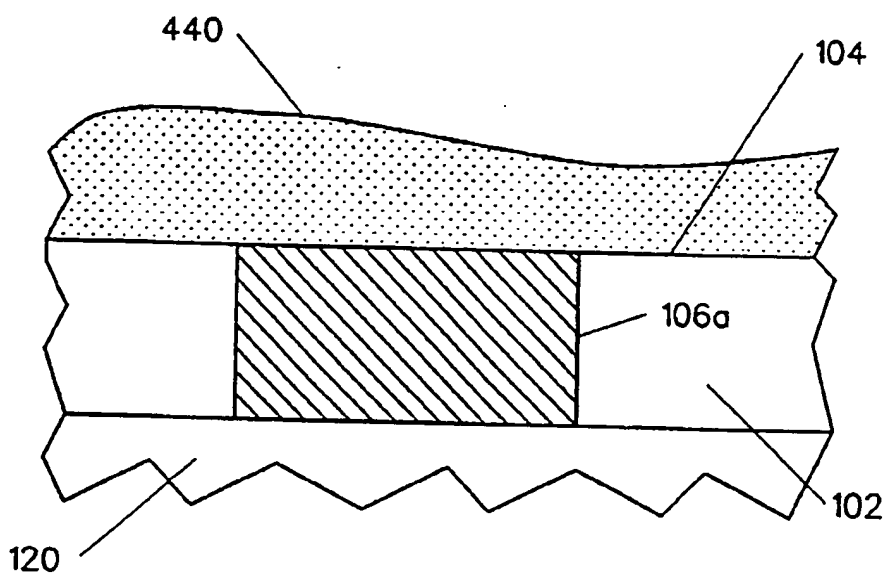


FIG. 4b

METHODS OF CLEANING SEMICONDUCTOR SUBSTRATES AFTER POLISHING

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of U.S. patent application Ser. No. 08/014,432, filed on Feb. 5, 1993, now abandoned by Rostoker.

TECHNICAL FIELD OF THE INVENTION

The present invention relates to processing steps in the fabrication or re-fabrication (e.g., repair) of semiconductor devices (e.g., wafers) and, more particularly, to the partial or complete polishing (stripping away) of layers previously deposited on the semiconductor device and, still more particularly, to the cleaning of the semiconductor device (e.g., wafer) after polishing.

BACKGROUND OF THE INVENTION

Semiconductor devices are fabricated step-by-step, beginning with a silicon wafer (substrate), implanting various ions, creating various circuit structures and elements, and depositing various insulating and conductive layers. Some of these layers are subsequently patterned by photoresist and etching, or similar processes, which results in topological features on the surface of the substrate. Subsequent layers over the topological layers inherit, and sometimes exacerbate, the uneven topology of the underlying layers. Such uneven (irregular, non-planar) surface topology can cause undesirable effects and/or difficulties in the application of subsequent layers and fabrication processes.

Hence, it is known, at various stages of semiconductor fabrication, to planarize a layer. Various techniques for planarizing a layer by etching or chemical-mechanical ("chem-mech") polishing are known. For example, chem-mech polishing of a semiconductor substrate is disclosed in U.S. Pat. Nos. 4,671,851, 4,910,155 and 4,944,836, incorporated by reference herein.

The present invention is directed to chem-mech polishing processes, which generally involve "rubbing" a wafer with a polishing pad in a slurry containing both an abrasive and chemicals. Typical slurry chemistry is KOH (Potassium Hydroxide), having a pH of about 11. A typical silica-based slurry is "SC1" available from Cabot Industries. Another slurry based on silica and cerium (oxide) is Rodel "WS-2000".

It is also known to use mechanical or chemical-mechanical (chem-mech) polishing techniques to completely remove (rather than to partially remove, or planarize) a layer that has been deposited. For example, U.S. Pat. No. 5,142,828, incorporated by reference herein, describes a process whereby a defective metallization layer is removed from the top of an electronic component such as an integrated circuit or a copper/polyimide substrate by polishing with a rotating pad and a slurry. Non-defective underlying metallization layers are preserved, and a new metallization layer is fabricated to replace the defective layer. For example, mechanical polishing of a copper layer, in a customizable high density copper/polyimide substrate, using a slurry of alumina grit with alumina particles between 0.05-3.0 microns suspended in solution, is disclosed in this patent. Slurries using silicon carbide and diamond paste are also described in the patent. The polishing of a tungsten layer is also suggested in the patent.

The aforementioned U.S. Pat. No. 4,910,155 discloses wafer flood polishing, and discusses polishing using 0.06 micron alumina particles in deionized water. The use of silica particulates is also discussed. Particulates of sizes as small as 0.006 microns (average size), and as large as 0.02 microns are discussed in this patent. The use of SiO₂ particulates (average diameter of 0.02 microns) suspended in water is also discussed in this patent.

Generally, chem-mech polishing is known for planarizing dielectric films. Generally, the penultimate layers of an integrated circuit are alternating dielectric and conductive layers forming interconnects, and the ultimate layer is a passivation layer, such as phosphosilicate glass (PSG). It is generally inconvenient and impractical to check the device at each step in the process since 1) functionally, the various gates and structures may not be interconnected at a particular stage, and 2) it is generally undesirable to remove the wafer from the "clean" fabrication environment at intermediate steps.

U.S. Pat. No. 4,956,313 discloses a via-filling and planarization technique. This patent discusses a planarization etch to remove portions of a metal layer lying outside of vias, while simultaneously planarizing a passivation layer, to provide a planarized surface upon which subsequent metal and insulator layers can be deposited. The use of an abrasive slurry consisting of Al₂O₃ particulates, de-ionized water, a base, and an oxidizing agent (e.g., hydrogen peroxide) is discussed, for etching tungsten and BPSG.

In the process of manufacturing semiconductor devices from silicon wafers, there is always the possibility that the device (or entire wafer) will be mis-manufactured. For example, a top metal layer (M_n) may exhibit voids reducing the cross-sectional area of conductive lines. Various other problems such as corrosion, mechanical stress and incomplete etching may be encountered. In the main hereinafter, voids in metal lines are discussed as an exemplary fault needing repair. Reference is made to "Stress Related Failures Causing Open Metallization, by Groothuis and Schroen, IEEE/IRPS, 1987, CH2388-7/87/0000-0001, pp.1-7, incorporated by reference herein.

Once a fault is identified, it can sometimes be repaired, and techniques such as focussed ion beam "micro-surgery" are known. However, in order to advantageously employ these repair techniques, or to remanufacture a defective layer it is necessary to strip off one or more of the top layers (e.g., passivation, metal, dielectric) of the device. These stripping techniques have as their goal returning the device (or a plurality of devices, when an entire wafer is processed in this manner) to a pre-existent, incomplete stage of manufacture, from which point onward, the device can be repaired or remanufactured.

Wet etching is one known technique for removing (stripping) layers of material in semiconductor devices. However, wet etching cannot be made to etch in any way except isotropically, which means that structures will be distorted in the horizontal (lateral) extent. Further, wet etching of oxide can destroy metal lines and bond pads.

Plasma etching, on the other hand, can be either isotropic or anisotropic, but it is usually unable to continue etching through all of the layers of material (e.g., oxide removal in the presence of metal lines) in the same cycle. This limitation forces the use of a series of different plasma etch processes, and simply does not work satisfactorily. In many instances, insulating layers un-

derlying metal areas are also etched away, with the result that the metal lines will lift off.

U.S. Pat. No. 4,980,019, entitled ETCH-BACK PROCESS FOR FAILURE ANALYSIS OF INTEGRATED CIRCUITS, (Baerg et al.; Dec. 25, 1990) discloses a method for etching exposed dielectric layer portions of an integrated circuit device to expose an underlying metal layer, by reactive ion etching (RIE) of the passivation layer. The technique is directed to etching back a delidded integrated circuit device.

U.S. Pat. No. 4,609,809, incorporated by reference herein, discloses method and apparatus for correcting delicate wiring of IC device employing an ion beam.

These techniques are unsatisfactory in that they alter the topography of the devices while film (layer) removal is taking place. In other words, they do not return the device to a truly pre-existent stage of fabrication. Consequently, significant losses in device throughput are incurred.

In any case, after chem-mech polishing, the surface of the wafer must be cleaned of debris, residue and detritus, and the like.

DISCLOSURE OF THE INVENTION

It is therefore an object of the present invention to provide an improved technique for polishing semiconductor devices.

It is a further object of the present invention to provide an improved technique for planarizing layers in semiconductor devices, including removing excess material such as metal overfilling vias.

It is a further object of the present invention to provide an improved technique for polishing back or removing layers in semiconductor devices.

It is a further object of the present invention to provide an improved technique for polishing back or removing layers in a semiconductor device as a prelude to reworking or repairing a defective layer in the device.

It is a further object of the invention to provide a technique for removing top layers of a semiconductor device, without damaging pre-existing topology, returning the wafer, undamaged, to a truly pre-existing state.

It is a further object of the present invention to provide an improved technique for chemical-mechanical ("chem-mech") polishing of semiconductor devices.

It is a further object of the present invention to provide an improved technique for chem-mech planarizing layers in semiconductor devices, including removing excess material such as metal overfilling vias.

It is a further object of the present invention to provide an improved technique for chem-mech polishing back or removing layers in semiconductor devices.

It is a further object of the present invention to provide an improved technique for chem-mech polishing back or removing layers in a semiconductor device as a prelude to reworking or repairing a defective layer in the device.

It is a further object of the invention to provide a technique for removing top layers of a semiconductor device, by chem-mech polishing, without damaging pre-existing topology, returning the wafer, undamaged, to a truly pre-existing state.

It is a further object of the invention to provide a technique for cleaning polishing residue from a semiconductor device which is compatible with the above-mentioned objects.

It is a further object of the invention to provide a technique for cleaning polishing residue from a semiconductor device which is compatible with the above-mentioned objects and which does not significantly erode the polished surface of the semiconductor device.

It is a further object of the invention to provide a technique for cleaning polishing residue from a semiconductor wafer which effectively removes both detritus (debris from the polished layer) and residual polishing slurry, without significantly attacking the polished (e.g., planarized) surface of the semiconductor device.

According to the invention, a semiconductor wafer is polished using particles of Aluminum Oxide (Al_2O_3) or Silica (SiO_2). Preferably, the particles are in a colloidal "suspension".

According to a feature of the invention, the Aluminum Oxide particles are preferably "Alpha" (α) state, but other forms of Aluminum Oxide (e.g., Gamma state, or pure Al_2O_3) may be used.

According to a feature of the invention, the Silica may be amorphous SiO_2 .

According to a feature of the invention, the size of the particles is on the order of 30-100 nm (nanometers), preferably approximately 50 nm.

According to a feature of the invention, the particles are used in a chemical-mechanical (chem-mech) "slurry", for chem-mech polishing a substrate.

According to a feature of the invention, the particles are used to remove unwanted structures, such as metal layers) from a finished or in-process substrate.

According to a feature of the invention, the particles are used to polish polyimide films or CVD TEOS layers.

According to a feature of the invention, the particles are used to planarize a layer or layers of an in-process semiconductor device. Such layer(s) may be dielectric films and/or metal layers, and such planarizing includes removing excess material such as metal overfilling vias.

According to a feature of the invention, the particles are used to remove a layer (or layers) of an in-process or substantially completed semiconductor device. Such layer(s) may be dielectric films and/or metal layers. The removed layer(s) may or may not be re-applied to the semiconductor device (substrate).

Preferably, an entire semiconductor wafer containing a plurality of semiconductor devices is polished with the particles, but individual dies (devices) can also be subjected to polishing with the particles.

According to a feature of the invention, the process of removing material from a semiconductor substrate with the particles is "surface-referenced", and the material removal process can be tailored to produce a resulting substrate surface which is either substantially planar or which is substantially conformal to underlying layers.

According to a feature of the invention, wafers which have been mis-manufactured can be returned to a pre-existing state, for repair (i.e., repair of the defective layer, followed by re-applying the overlying layers) or partial re-manufacture (i.e., re-applying the stripped off defective layer and overlying layers).

The use of the particles for polishing is a very effective way to prepare wafers for repair in the Back-End (BE) process. In this process, wafers are substantially completed, and their value to the manufacturer is maximized. Scrapping the wafers is costly and the loss of time to manufacture replacement wafers is at it's worst. In this case, a polish process can remove dielectric films back to the level of the BPSG reflowed glass layer. This

removal can take place at the Metal 1 layer, Interlevel dielectric (ILD), Metal 2 or Passivation Layers. In each case, if the metal is exposed to the polishing slurry, the metal will be removed back to the level of the silicon contacts. In this case, it is most optimal to polish back to the BPSG level.

The use of tungsten plug technology during metallization has certain beneficial effects in connection with the disclosed use of polishing for repair. Tungsten is not particularly attacked by basic polishing slurry. As such, the polish process does not automatically knock the metal level back to the contact level when upper metal levels are exposed to polishing slurry.

Aluminum, on the other hand, such as may be found in metal layers, may be severely attacked by the polishing slurry. Preferably, when polishing an aluminum layer, it is polished back to the contact level, since it is relatively difficult to remove aluminum in a via.

According to the invention, polishing residue, which includes detritus (debris) from the polished layer and residue from the polishing slurry, can be effectively cleaned from the semiconductor device using a phosphoric acid cleaning solution. An aluminum oxide particulate is considerably more soluble in the phosphoric acid cleaning solution than in the more conventional hydrofluoric acid cleaning solution used to remove residue from polishing silica-based slurries.

The phosphoric acid solution can contain a small concentration of hydrofluoric acid relative to the concentration of phosphoric acid. The hydrofluoric acid component in the cleaning solution serves to dissolve and remove any silicon dioxide polishing debris (detritus), which may result (e.g., from having polished a silicon dioxide layer or structure on the wafer. The relatively low concentration of hydrofluoric acid compared to that of phosphoric acid limits the amount of erosion of the polished layer. The relative concentration (e.g., molar) of hydrofluoric acid compared to that of phosphoric acid in the cleaning solution is, for example, less than 25%, 20%, 10%, 5%, 2%, 1%, or $\frac{1}{2}\%$.

Other objects, features and advantages of the invention will become apparent in light of the following description thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1a is a cross-sectional view of a semiconductor device being polished, according to the present invention.

FIG. 1b is a cross-sectional view of the semiconductor device of FIG. 1a, after polishing.

FIG. 2a is a cross-sectional view of a semiconductor device being polished, according to the present invention.

FIG. 2b is a cross-sectional view of the semiconductor device of FIG. 2a, after polishing.

FIG. 3 is a cross-sectional view of a semiconductor device exhibiting a defect, according to the present invention.

FIG. 3a is a cross-sectional view of the semiconductor device of FIG. 3, after polishing.

FIG. 3b is a cross-sectional view of the semiconductor device of FIG. 3, after polishing.

FIG. 3c is a cross-sectional view of the semiconductor device of FIG. 3, after polishing.

FIG. 4a is an enlarged cross-sectional view of the semiconductor device of FIG. 1a, after polishing, showing a polishing residue.

FIG. 4b is a cross-sectional view of the semiconductor device of FIG. 4a, showing removal of the polishing residue.

It should be understood that while one semiconductor device may be shown and discussed, or only a particular portion thereof, the present invention is applicable to a plurality of such devices resident on a single silicon wafer.

DETAILED DESCRIPTION OF THE INVENTION

Technological progress is often based on the availability of new and improved materials which enable increasing the performance of new products or new methods of manufacture. For example, the discovery of the class of high temperature superconducting ceramics has given rise to numerous possible new products and new manufacturing methods. Frequently, progress in new material developments arises from the discovery of new chemical compounds or more sophisticated methods of manufacturing products, such as, new methods of miniaturization for use in integrated circuit manufacture.

Recently, methods have been developed for controllably producing ultrafine-grained, or nanocrystalline, materials (typically, about 1-100 nm grain diameters). These new methods have made possible the production of new materials having substantially different physical and chemical properties than the large grained, or single crystal, counterparts having substantially the same chemical composition.

U.S. Pat. No. 5,128,081, incorporated by reference herein, discloses a method of making nanocrystalline alpha alumina, and discusses providing substantially stoichiometric Al_2O_3 , and discusses providing nanocrystalline materials having selectable grain size. The patent discloses an apparatus for preparation of nanocrystalline or nanophase materials (hereinafter, "nanocrystalline" materials shall include crystalline, quasicrystalline and amorphous phases). The patent discusses the preparation of nanocrystalline aluminum oxide, with a treatment that results in transformation of nanocrystalline aluminum powders (likely with a very thin oxide coating) to the thermodynamically stable alpha phase of aluminum oxide having an average particle size of about 18 nm. The patent discusses forming preferentially alpha alumina nanocrystalline ceramic material having a grain size of less than about 20 nm, and discusses alpha alumina having a median grain size of about 18 nm.

Given the recent advances in methods of producing such nanocrystalline materials, numerous problems in areas such as polishing semiconductor substrates can now be addressed using these new nanocrystalline materials.

According to the invention, aluminum oxide (Al_2O_3) particles are used to polish a semiconductor substrate. (Alumina is any of several forms of aluminum oxide, Al_2O_3 , occurring naturally as corundum, in a hydrated form in bauxite, and with various impurities such as ruby, sapphire, and emery, and is used in aluminum production and in abrasives, refractories, ceramics, and electrical insulation.)

The aluminum oxide particles are preferentially substantially entirely in the alpha phase. The alpha phase of aluminum oxide is harder than other phases of aluminum oxide, such as the gamma phase.

The aluminum oxide is preferably used in a chem-mech slurry for polishing the semiconductor substrate. Characteristics of the polishing particles:

According to the invention, the alpha aluminum oxide particles used for polishing exhibit the following characteristics. Preferably, the particle size is "X" nm, and the distribution of particle sizes is controlled to within "Y" nm, and the particles used for polishing are "Z" percent (%) in the alpha phase, where:

"X" is 10-100 nm; such as 10, 20, 30, 40 or 50 nm, and is preferably no greater than 50 nm; and

"Y" is approximately "P" percent of "X", where "P" is 10%, 20%, 30%, 40% or 50%, and is preferably no greater than 50% to ensure a narrow (Gaussian) distribution of particle sizes about "X";

"Z" is at least 50%, including at least 60%, 70%, 80% and 90%, and as high as 100%.

A quality factor "Q" is inversely related to "Y", and is a measure of the distribution of particle sizes. "Q" can be calculated as the concentration of particles at the desired size "X", divided by the range of sizes of particles at 3 db (decibels) lower than "X". Preferably, the size distribution of alpha aluminum oxide particles used for polishing exhibits a "Q" of at least 10, including 10, 50, 100, 500, 1000, 5000, or 10,000 ("Q" is dimensionless).

According to the invention, aluminum oxide particles exhibiting the aforementioned characteristics are used for planarizing a layer of a semiconductor device, such as an interlevel dielectric layer, a polyimide film, or a plasma etched CVD TEOS.

According to the invention, aluminum oxide particles exhibiting the aforementioned characteristics are used for stripping away a top metal layer, which may have been defectively applied to the semiconductor device.

According to the invention, aluminum oxide particles exhibiting the aforementioned characteristics are advantageous for use in polishing semiconductor devices because they can be supplied in a neutral state, then acidified or baseified at will, depending upon the layer to be polished. For maximum performance in polishing thermal oxide, a pH of 10.5 to 11 is desirable. For polishing metals, pH's as low as 3.0 to 3.5 are preferred.

Aluminum oxide exhibiting the aforementioned characteristics is superior to colloidal silica, since acidification of colloidal silica results in flocculation. Aluminum oxide remains in suspension under a wide range of pH's.

For polishing an aluminum layer, it is preferred to acidify aluminum oxide exhibiting the aforementioned characteristics with zinc sulphate. Increased acidification with alum is preferred. Glacial acetic acid is recommended for polishing other materials.

According to the invention, maintaining a high "Q" range of high percentage alpha phase aluminum oxide particles ensures superior polishing. For example, particles significantly larger than "X" tend to scratch the surface being polished, and particles significantly smaller than "X" are less effective in polishing and tend to dilute the slurry with relatively useless material.

In an alternate embodiment of the invention, gamma aluminum oxide is substituted for the alpha aluminum oxide described above.

In yet another embodiment of the invention, a colloidal suspension of amorphous silica is substituted for the alpha aluminum oxide described above.

Polishing to planarize:

FIG. 1a shows an in-process semiconductor device 100 having an layer 102 exhibiting a non-planar top surface 104. For example, the layer 102 is an interlevel dielectric layer (ILD) overlying a metal layer 106 having topological features such as conductive lines 106a, 106b and 106c. Prior to forming vias (not shown) through the ILD layer 102, it is desirable to planarize the top surface 104 of the layer 102. Hence, FIG. 1a shows a polishing pad 110 positioned to planarize the top surface 104 of the layer 102. A medium 112 containing particles (shown as dots ".") of alpha aluminum oxide is interposed between the polishing pad 110 and the top surface 104 of the layer 102. The layers 102 and 104 are formed atop a substrate 120.

FIG. 1b shows the semiconductor device 100 of FIG. 1a, after polishing. As shown, the top surface 104 of the layer 102 is substantially planar.

Polishing to remove excess material:

FIG. 2a shows an in-process semiconductor device 200 having a thick interlevel dielectric (ILD) layer 202 overlying a patterned metal layer 206 having conductive lines 206a, 206b and 206c. Vias 208 are formed through the ILD layer 202, in line with selected conductors 206a,b,c. A layer of metal 209 is applied over the ILD 202, to fill the vias 208, for interconnecting the lines 206a,b,c to a subsequent patterned layer of metal (not shown) overlying the ILD 202. At this point, it is desirable to remove the excess metal 209 overfilling the vias 208. Hence, FIG. 2a shows a polishing pad 210 positioned to remove the excess metal, while planarizing the top surface of the in-process substrate 220. A medium 212 containing particles (shown as dots ".") of alpha aluminum oxide is interposed between the polishing pad 210 and the top surface of the layer 209.

FIG. 2b shows the semiconductor device 200 of FIG. 2a, after polishing. As shown, the top surface of the layer 202 is substantially planar, the vias 208 are perfectly filled with metal 209, and there is no excess metal 209 outside of the vias 208.

Polishing to strip a layer:

FIG. 3 shows an idealized, substantially completed semiconductor device 300 displaying a defect. In this case open (or partially open) metallization will be discussed as a "generic" defect requiring re-working or repair of the device 300.

By way of example, in the fabrication process, the following steps proceed sequentially. First, lower layers 314 are deposited, patterned and the like on a substrate 312. The lower layers include any of a variety of depositions forming circuit structures, contacts and elements, as is known.

Next, by way of example, a layer 316 of Borophosphosilicate glass (BPSG) is deposited, which is a known technique for creating an intermediate planar topology for subsequent metal deposition.

Vias may be formed through the BPSG layer 316 to the lower layers 314, and filled by overlying metal. Alternatively, as shown, a tungsten plug 318 is formed atop the lower layers 314.

Next, a first, patterned metal layer ("M1") 320, formed of aluminum or an aluminum alloy, is deposited, creating a pattern of conductive lines.

Next, an intermetal insulating layer (ILD dielectric film) 322 is deposited. A via 324 is formed through the dielectric film 322 and through the BPSG layer 316 for connection of overlying metal to the lower layers 314.

Next, a second, patterned metal layer ("M2") 326, again formed of aluminum or an aluminum alloy, is

deposited, creating a pattern of conductive lines and filling the via 324.

As shown, the second metal layer 326 contains a void 328, which is a manufacturing defect generally undetectable at this stage of manufacturing.

Finally, a passivation layer 330, such as phosphosilicate glass (PSG) is deposited.

The resulting, substantially completed device can now be functionally tested. Such testing is expected to reveal the existence of the defect 328, and having been located and diagnosed, the task remains to strip off the passivation layer 330 and possibly the second metal layer 326 to repair or re-manufacture the second metal layer, respectively. To this end, the device 310 is subjected to chemi-mechanical polishing, as in FIGS. 1a and 2a.

FIG. 3a shows the device 300 after polishing, according to one embodiment of the invention. In this embodiment, the passivation layer 330 has been stripped (polished back) to the level of the second metal layer 326. At this point, it is possible to repair the defect 328 using a focussed ion beam, or other suitable repair technique.

FIG. 3b shows the device 300 after polishing, according to another embodiment of the invention. In this embodiment, the passivation layer 330 and the second metal layer 326 have both been stripped (polished back) to the level of the intermetal dielectric film 322. It would be expected that the metal in the via 324 would disappear if it is of the same material (aluminum) as that of the second metal layer 326. If the material in the via 324 is not severely attacked, it is possible to remanufacture (redeposit) the second metal layer (including any material removed from the via 324) and the passivation layer.

FIG. 3c shows the device 300 after polishing, according to yet another embodiment of the invention. In this embodiment, the passivation layer 330, the second metal layer 326, the intermetal dielectric film 322 and the first metal layer 320, in other words all of the upper layers, have been stripped (polished back) to the level of the BPSG layer 316. In this example, the tungsten plug 318 is exposed, but with most common polishing slurries (e.g., Cabot Industries Type SC-1) the tungsten will not be attacked.

Evidently, it is possible to polish back all the way to the contact level. In any case, the device 300 was substantially completely manufactured prior to polish back for repair. It is also possible that the polishing back technique could be applied at a somewhat earlier step, such as after deposition of first metal. By "substantially complete", it is meant that the fabrication of the device has proceeded to at least deposition of first metal.

Having thus described various applications for polishing semiconductor devices, there are set forth some exemplary polishing media.

EXAMPLE 1

In this example, a medium of aluminum oxide particles having the following characteristics is employed for polishing a semiconductor substrate: "X" = 50 nm; "Y" = 50%; and "Z" = 50%, and is used for chem-mech polishing, such as is set forth in any of the exemplary applications for chem-mech polishing (see Figures).

EXAMPLE 2

In this example, a medium of aluminum oxide particles having the following characteristics is employed for polishing a semiconductor substrate: "X" = 50 nm;

"Z" = 50%; and "Q" = 100, and is used for chem-mech polishing, such as is set forth in any of the exemplary applications for chem-mech polishing (see Figures).

EXAMPLE 3

In this example, a medium of aluminum oxide particles having the following characteristics is employed for polishing a semiconductor substrate: "X" = 10 nm; "Y" = 10%; and "Z" = 90%, and is used for chem-mech polishing, such as is set forth in any of the exemplary applications for chem-mech polishing (see Figures).

EXAMPLE 4

In this example, a medium of aluminum oxide particles having the following characteristics is employed for polishing a semiconductor substrate: "X" = 10 nm; "Z" = 90%; and "Q" = 1000, and is used for chem-mech polishing, such as is set forth in any of the exemplary applications for chem-mech polishing (see Figures).

EXAMPLE 5

As mentioned hereinabove, other phases of aluminum oxide, as well as silica, especially amorphous silica, can be substituted for the alpha phase, according to any of the previous examples.

Cleaning of the Semiconductor Device After Polishing

It is well known that after polishing a semiconductor device (e.g., 100, FIG. 1a; 200, FIG. 2a) to remove all or a portion of a layer (e.g., 104, FIG. 1a, 209, FIG. 2a), a film residue is left behind which must be cleaned. The film residue is composed primarily of the polishing slurry (e.g., 112, FIG. 1a; 212, FIG. 2a) and "detritus," or fine debris from the material of the layer which was polished. This is illustrated in FIG. 4.

FIG. 4a show a portion of the semiconductor device 100 (see FIG. 1b) after polishing. The ILD layer 102 has been polished back to a point where the conductive line 106a is exposed and flush with the surface 104 of the ILD layer 102. After polishing, however, a thin film of residue 430 remains. This residue comprises loose debris (detritus) from the polished layer 102 (and perhaps some detritus from the conductive line 106a) and leftover polishing medium and loose polishing particulate matter (e.g., aluminum oxide).

The effectiveness of subsequent processing of the semiconductor device 100 and the ultimate quality of the finished integrated circuit are dependent, in part, upon effective removal (cleaning) of the residue from the wafer. It is possible to remove at least part of the residue by simply "rinsing" the semiconductor device 100, because the residue comprises, in large part, loose particulate matter. However, such "rinsing" cannot guarantee complete cleansing of the wafer surface, and may leave "stubborn" particulate residue behind. Any extraneous matter (e.g., residue 430) remaining on the semiconductor device 100 after polishing has an adverse effect on subsequent processing steps. Evidently, more complete removal of the residue is required.

When polishing compounds based on silicon dioxide (silica) are used, it is known to remove the film residue (e.g., 430) by "washing" the semiconductor device with hydrofluoric acid. The silicon dioxide particles in the slurry is highly soluble in hydrofluoric acid, facilitating thorough removal of all of the slurry residue. If the layer being polished is also silicon dioxide, then the debris (detritus) from the polished layer will also be dissolved (and washed away). However, a certain amount of the exposed surface of the layer itself may

also be attacked by the hydrofluoric acid wash. It is evidently somewhat undesirable to remove material from the polished layer after the polishing process has terminated, since this would introduce an uncertainty into a process that is geared towards providing a polished surface of known characteristics.

When polishing compounds such as those described hereinabove (e.g. slurries based upon aluminum oxide particulate) or other polishing compounds based on polishing particles other than silicon dioxide are used, the effectiveness of cleaning with hydrofluoric acid is somewhat attenuated. These residual materials can be significantly less soluble in hydrofluoric acid than the material being polished, in which case the layer that was polished may be attacked more vigorously by the hydrofluoric acid than is the slurry residue. This can potentially lead to significant loss of layer thickness without effective removal of the polishing residue.

For polishing slurries based upon aluminum oxide and related materials, the polishing slurry and detritus can be effectively removed by using phosphoric acid or a solution of phosphoric acid and hydrofluoric acid. ("Related materials," in this context, means any polishing material which is relatively highly soluble in phosphoric acid). Aluminum oxide, for example, is effectively dissolved by the phosphoric acid, without significant dissolution of silicon dioxide. In other words, slurry residue containing aluminum oxide can effectively be removed without damaging an exposed layer of silicon dioxide (for example). The addition of small quantities of hydrofluoric acid to make a cleaning solution of phosphoric acid and hydrofluoric acid provides for removal of the silicon dioxide detritus, thereby cleaning the semiconductor device more effectively than by using only hydrofluoric acid or by using only phosphoric acid.

In FIG. 4b a cleaning solution 440 is disposed over the semiconductor device 100, substantially dissolving the film residue 430, while leaving the underlying ILD layer 102 relatively untouched. The cleaning solution 440 is primarily phosphoric acid. Assuming, however, that the ILD layer 102 is silicon dioxide, then a small amount of hydrofluoric acid is mixed with the phosphoric acid, to dissolve residual silicon dioxide detritus. As before, the hydrofluoric acid may attack the now-polished and exposed surface of the ILD layer. However, by limiting the amount of hydrofluoric acid, this effect can be minimized.

The cleaning solution 440 can be either purely phosphoric acid (e.g., in some concentration, such as 10%, 20%, etc.), or can be a mixture of phosphoric acid and hydrofluoric acid containing a relatively low concentration of hydrofluoric acid. For example, there may be $\frac{1}{2}$ %, 1%, 2%, 5%, 10%, 20%, or 25% relative concentration of hydrofluoric acid vis-a-vis phosphoric acid in the cleaning solution for use in washing polishing residue from the surface of a semiconductor wafer. In any case, when polishing a layer of one material (e.g., silicon dioxide) with a slurry containing a different material (e.g., alumina), the cleaning solution contains at least a relatively high concentration of a solvent which is selective to the slurry residue, and a relatively small amount of a different solvent which is selective to the layer detritus.

What is claimed is:

1. A method of cleaning polishing residue from a semiconductor device, comprising:
providing a semiconductor device;

chemical-mechanically polishing a surface of the semiconductor device with an alumina-containing slurry, thereby leaving a polishing residue over the surface; and

cleaning the surface of the semiconductor device with a cleaning solution consisting essentially of a solution of phosphoric acid and hydrofluoric acid.

2. A method according to claim 1, wherein:
the cleaning solution has a relatively low concentration of hydrofluoric acid, as compared to the concentration of phosphoric acid.
3. A method according to claim 2, wherein:
the concentration of hydrofluoric acid, as compared to the concentration of phosphoric acid in the solution, is less than 25%.
4. A method according to claim 2, wherein:
the concentration of hydrofluoric acid, as compared to the concentration of phosphoric acid in the solution, is less than 20%.
5. A method according to claim 2, wherein:
the concentration of hydrofluoric acid, as compared to the concentration of phosphoric acid in the solution, is less than 10%.
6. A method according to claim 2, wherein:
the concentration of hydrofluoric acid, as compared to the concentration of phosphoric acid in the solution, is less than 5%.
7. A method according to claim 2, wherein:
the concentration of hydrofluoric acid, as compared to the concentration of phosphoric acid in the solution, is less than 2%.
8. A method according to claim 2, wherein:
the concentration of hydrofluoric acid, as compared to the concentration of phosphoric acid in the solution, is less than 1%.
9. A method according to claim 2, wherein: the concentration of hydrofluoric acid, as compared to the concentration of phosphoric acid in the solution, is less than $\frac{1}{2}$ %.
10. Method of polishing a substrate, comprising:
polishing the surface of a semiconductor substrate with a medium of aluminum oxide particles having a preferred size "X" nanometers, a range of sizes within "Y" nanometers of "X" and a percentage "Z" of particles in the alpha phase, wherein:
"X" is 10-100 nm;
"Y" is "P" percent of "X", where "P" is no greater than 50%; and
"Z" is at least 50%; and
cleaning the surface of the semiconductor substrate with a cleaning solution consisting essentially of phosphoric acid and hydrofluoric acid.
11. A method according to claim 10, wherein:
the phosphoric acid solution has a concentration of hydrofluoric acid relative to that of phosphoric acid of less than 25%.
12. A method according to claim 11, wherein:
the phosphoric acid solution has a concentration of hydrofluoric acid relative to that of phosphoric acid of less than 20%.
13. A method according to claim 11, wherein:
the phosphoric acid solution has a concentration of hydrofluoric acid relative to that of phosphoric acid of less than 10%.
14. A method according to claim 11, wherein:
the phosphoric acid solution has a concentration of hydrofluoric acid relative to that of phosphoric acid of less than 5%.

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15. A method according to claim 11, wherein:
the phosphoric acid solution has a concentration of
hydrofluoric acid relative to that of phosphoric
acid of less than 2%.
16. A method according to claim 11, wherein:
the phosphoric acid solution has a concentration of
hydrofluoric acid relative to that of phosphoric
acid of less than 1%.
17. A method according to claim 11, wherein:
the phosphoric acid solution has a concentration of
hydrofluoric acid relative to that of phosphoric
acid of less than $\frac{1}{2}$ %.
18. Method of cleaning chemical-mechanical polish-
ing residue, including polishing slurry and substrate
detritus, from a surface of a semiconductor wafer that
has been chemical-mechanically polished, comprising:
providing a cleaning solution of a first amount of
phosphoric acid and second amount of hydroflu-
oric acid, and no other acid, wherein the second
amount is less than 25% of the first amount; and

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- cleaning the surface of the semiconductor wafer with
the cleaning solution.
19. Method, according to claim 18, wherein:
the polishing slurry contains alumina particles having
a size less than 50 nm; and
the alumina particles are primarily in the alpha phase.
20. Method, according to claim 18, wherein:
the second amount is less than 20% of the first
amount.
21. Method, according to claim 18, wherein:
the second amount is less than 10% of the first
amount.
22. Method, according to claim 18, wherein:
the second amount is less than 5% of the first amount.
23. Method, according to claim 18, wherein:
the second amount is less than 2% of the first amount.
24. Method, according to claim 18, wherein:
the second amount is less than 1% of the first amount.
25. Method, according to claim 18, wherein:
the second amount is less than $\frac{1}{2}$ % of the first amount.

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United States Patent [19]

Atsugi et al.

[11] Patent Number: 5,868,604

[45] Date of Patent: Feb. 9, 1999

[54] ABRASIVES COMPOSITION, SUBSTRATE AND PROCESS FOR PRODUCING THE SAME, AND MAGNETIC RECORDING MEDIUM AND PROCESS FOR PRODUCING THE SAME

[75] Inventors: Takeshi Atsugi; Manabu Shibata, both of Tochigi-ken; Tsutomu Koseki, deceased, late of Tochigi-ken, all of Japan, by Yoshitada Koseki, Tomiko Koseki, heirs

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[21] Appl. No.: 744,142

[22] Filed: Nov. 12, 1996

[30] Foreign Application Priority Data

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Mar. 27, 1996	[JP]	Japan	8-071577

[51] Int. Cl.⁶ B05D 5/00; C01F 7/02; C09G 1/02; C23C 22/05

[52] U.S. Cl. 451/36; 51/309; 106/1.05

[58] Field of Search 51/307, 308, 309; 451/36; 427/355; 106/1.05, 286.5

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[57] ABSTRACT

An abrasives composition comprises (i) one or more abrasives, (ii) one or more abrasion accelerators and (iii) water. The abrasive comprises intermediate alumina particles having a mean particle size of primary particles of 40 nm or less.

13 Claims, 1 Drawing Sheet

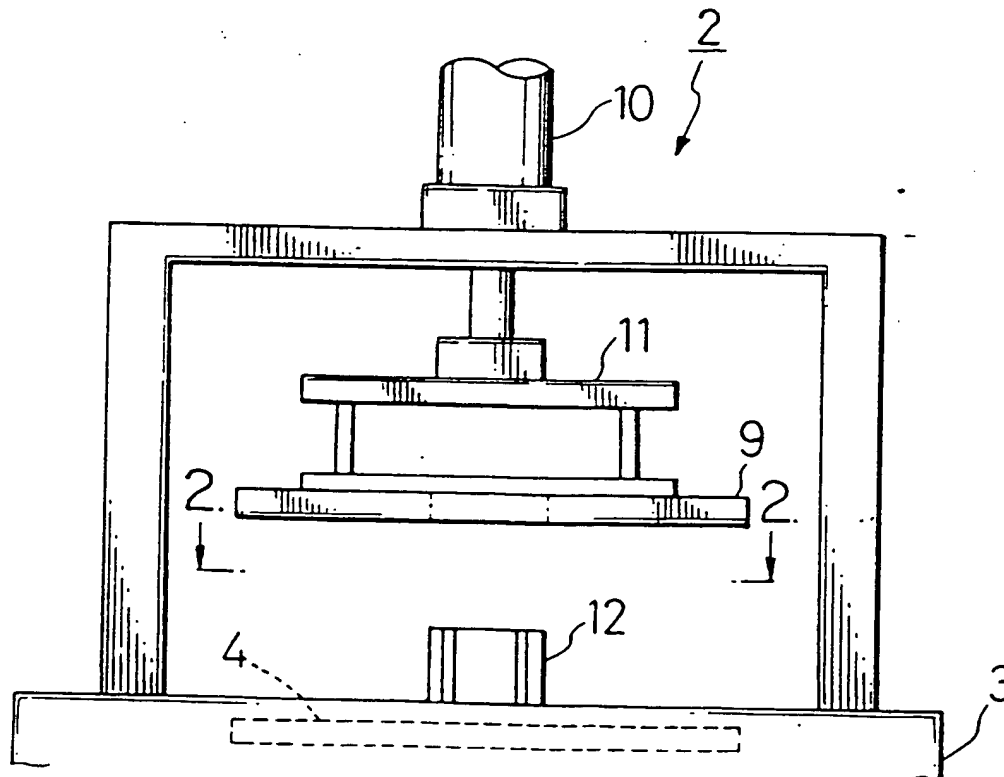


Fig. 1

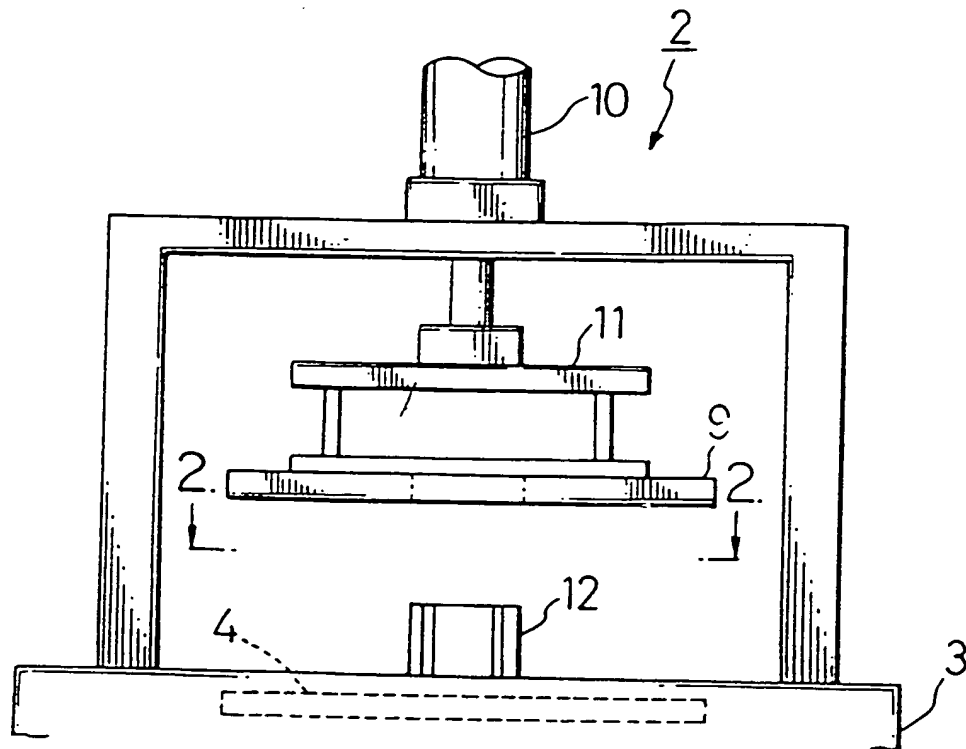
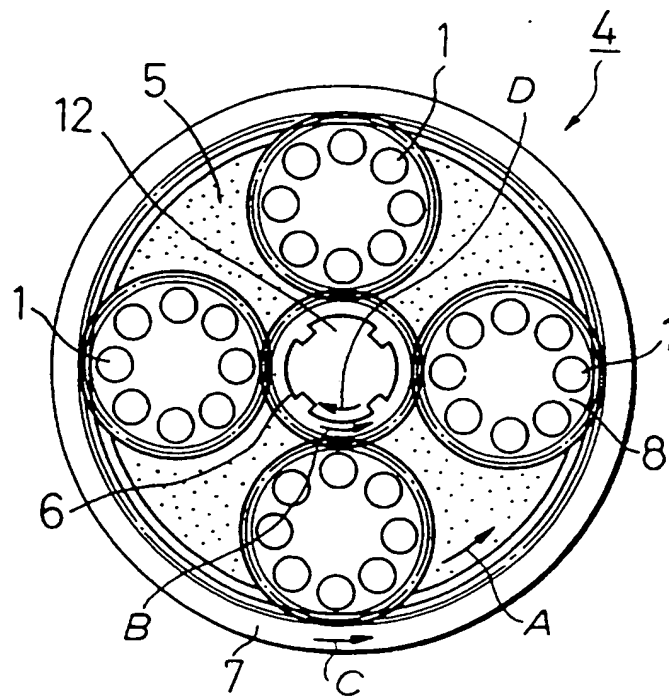


Fig. 2



ABRASIVES COMPOSITION, SUBSTRATE AND PROCESS FOR PRODUCING THE SAME, AND MAGNETIC RECORDING MEDIUM AND PROCESS FOR PRODUCING THE SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to an abrasives composition. This invention particularly relates to an abrasives composition capable of producing a substrate for a magnetic recording medium, which substrate has a very small value of surface roughness. This invention also relates to a process for producing a substrate, wherein the abrasives composition is used. This invention further relates to a glass-like carbon substrate for a magnetic recording medium, wherein the substrate has a very small value of surface roughness, and a magnetic recording medium using the glass-like carbon substrate.

2. Description of the Related Art

Recently, most computers are provided with recording devices, such as magnetic disk drives. With the increase in the amount of recorded information occurring in recent years, it is required that recording devices be capable of recording information at high densities. The magnetic disk drive has a magnetic head and a magnetic disk. As a means for achieving the recording of information at high densities, it is necessary to reduce the glide height of the magnetic head. For such purposes, it is necessary that the surface roughness (Ra) of the magnetic disk be as small as possible.

Recently, glass-like carbon substrates have attracted particular attention as substrates for magnetic disks. The glass-like carbon substrates have a hardness higher than aluminum substrates, which are currently popular as the substrates for magnetic disks. Therefore, the thickness of the substrates can be reduced when made of glass-like carbon. Also, glass-like carbon has a small specific gravity and is light in weight, and therefore glass-like carbon substrates are light in weight. Accordingly, substrates are very suitable for use in computers, which should be kept small in size and light in weight.

However, when glass-like carbon substrates are used as substrates for magnetic disks, it is difficult for the surface roughness of the glass-like carbon substrates to be reduced, due to the high hardness of the glass-like carbon. Specifically, if γ -alumina particles, typically used, are used in polishing step carried out during the production of the substrates for magnetic disks, the surface roughness of the substrates cannot be reduced (e.g., to less than 4 Å). This is because the α -alumina particles are hard and the mean particle size of their primary particles is at least 0.1 μ m. If very soft abrasive is used in lieu of α -alumina particles, sufficient abrasive effects cannot be obtained, and the surface roughness cannot be reduced.

Japanese Patent Application Laid-Open 7-240025 proposes a method for reducing the surface roughness of a magnetic disk substrate. The method comprises the step of corroding a substrate material with a chemical corrosive agent, which reacts with the substrate material and softens a portion of the substrate material, and the step of abrading and removing this portion of the substrate material using colloidal particles. Also proposed is a magnetic disk substrate having a surface roughness of less than 4 Å. However, it is difficult to reduce the surface roughness of a glass-like carbon substrate to less than 4 Å with the method proposed in this patent application.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an abrasives composition capable of imparting a low surface roughness to a substrate, particularly a glass-like carbon substrate, so that information can be recorded on the magnetic recording medium at high densities.

Another object of the present invention is to provide a substrate, in particular a substrate for a magnetic recording medium, having a very low surface roughness, and a process for producing the substrate.

The inventors carried out extensive research in order to achieve these objects and found that the surface of a substrate can be efficiently processed to the super-polished state by an abrasives composition containing specific alumina particles. The present invention is based on these findings.

The present invention provides an abrasives composition, comprising:

- (i) one or more abrasives,
- (ii) one or more abrasion accelerators, and
- (iii) water,

wherein the abrasives comprise intermediate alumina particles having a mean particle size of primary particles of 40 nm or less.

The present invention also provides a process for producing a substrate, comprising:

abrading surfaces of said substrate with an abrasives composition,

wherein said abrasives composition comprises

- (i) one or more abrasives,
- (ii) one or more abrasion accelerators, and
- (iii) water, and

said abrasives comprise an intermediate alumina particle having a mean particle size of primary particles of 40 nm or less.

The present invention further provides a substrate, comprising glass-like carbon, wherein said substrate has a surface roughness Ra of less than 4 Å.

The present invention still further provides a magnetic recording medium, comprising:

- (i) the above-mentioned glass-like carbon substrate,
- (ii) a magnetic layer on said substrate, and
- (iii) a protective layer on said magnetic layer.

With the abrasives composition in accordance with the present invention, wherein the abrasives comprise the intermediate alumina particles having a mean particle size of primary particles of 40 nm or less, a low surface roughness can be imparted to the substrate, so that information can be recorded on the magnetic recording medium at high densities.

In particular, with the abrasives composition in accordance with the present invention, high-hardness substrates, e.g. glass-like carbon substrates, for which the super-polishing process ordinarily cannot easily be carried out, can be processed such that the surface roughness of the abraded substrates may be less than 4 Å, providing very smooth surfaces.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic front view showing a double-sided polishing machine, which may be used in a polishing step for a substrate for a magnetic recording medium; and

FIG. 2 is a view taken along line X—X of FIG. 1.

DETAILED DESCRIPTION OF THE INVENTION

Firstly, the abrasives composition in accordance with the present invention will be described in detail.

As described above, the abrasives composition in accordance with the present invention contains, as essential components, water, an abrasive and an abrasion accelerator. Also, the abrasives composition in accordance with the present invention is characterized by using, as the abrasive, one or more intermediate alumina particles having a mean particle size of primary particles of 40 nm or less. The features of the abrasives composition in accordance with the present invention will be described hereinbelow.

The abrasive used is an intermediate alumina particle having a mean particle size of primary particles of 40 nm or less. The term "intermediate alumina particle" as used herein means alumina particles other than α -alumina particles. Specifically, examples of intermediate alumina particle include γ -alumina particles, θ -alumina particles, δ -alumina particles, η -alumina particles, and amorphous alumina particles. If a substrate, particularly a high-hardness substrate (e.g., a glass-like carbon substrate) is abraded using α -alumina particles as the abrasive, it will be difficult for the surface roughness of the abraded substrate to be reduced to a very small value (e.g., less than 4 Å). (Ordinarily, in such cases, the surface roughness of the abraded substrate is reduced to 10 Å at the lowest.) This is because the α -alumina particles are hard and their mean particle size is 0.1 μ m or more. Alternatively, if the abrasive processing is carried out so that the surface roughness of the abraded substrate may become very small, the time required to carry out the abrasive processing will become very long, and pits are liable to occur on the surface of the abraded substrate. In contrast, when the intermediate alumina particle is used as the abrasive, the surface roughness of the abraded substrate can be reduced (e.g., less than 4 Å) without any defects on the surface of the abraded substrate. The above-enumerated types of the intermediate alumina particle may be used alone, or two or more may be used in combination. Among the above-enumerated types of intermediate alumina particles, the γ -alumina particles and the θ -alumina particles are preferable, and the γ -alumina particles are particularly preferable.

The mean particle size of the primary particles of the intermediate alumina particle is 40 nm or less. If the mean particle size of the primary particles of the intermediate alumina particle is larger than 40 nm, it will become difficult for the surface roughness of the abraded substrate to be reduced (e.g., less than 4 Å) when the abrasive processing is carried out on the substrate, particularly a substrate having high hardness, such as a glass-like carbon substrate. No particular limitation is imposed upon the lower limit of the particle size of the intermediate alumina particle. However, if the particle size of the intermediate alumina particle is very small, the abrasion speed will become slow, and the production efficiency will become low. Therefore, the mean particle size of the primary particles of the intermediate alumina particle is preferably at least 10 nm. The mean particle size of the primary particles of the intermediate alumina particle is more preferably 15 to 30 nm.

The intermediate alumina particle having a mean particle size of primary particles of 40 nm or less, e.g. the γ -alumina particles, can be produced by the known technique of heating ammonium alum $[\text{NH}_4\text{Al}(\text{SO}_4)_2]$ up to 900° C. Also known to persons skilled in the art is that the intermediate alumina particle can also be easily produced with any one of various other techniques. The intermediate alumina particle is commercially available under the trade name "0.02CR" (primary particle size: 0.02 μ m, supplied by BAIKOWSKI JAPAN CO.).

The mean particle size of the primary particles of the intermediate alumina particle may be measured by adding a

dispersing agent to 0.1 g of the intermediate alumina particle, dispersing the intermediate alumina particle by subjecting to ultrasonic waves, drying the resulting dispersion, observing the dried intermediate alumina particle with a scanning electron microscope (SEM), and carrying out image analysis.

The intermediate alumina particle is used in the so-called "slurry state," in the abrasives composition in accordance with the present invention. The content of the intermediate alumina particle in the abrasives composition in accordance with the present invention may be selected in accordance with the viscosity of the abrasives composition, the quality required for the product, or the like. Generally, the content of the intermediate alumina particle in the abrasives composition in accordance with the present invention preferably is 0.05% to 30%, by weight, and more preferably 0.3% to 25%, by weight. When the content of the intermediate alumina particle in the abrasives composition in accordance with the present invention falls within the aforesaid range, a substrate having a low surface roughness (e.g., a surface roughness of less than 4 Å) can be obtained with good production efficiency.

No limitation is imposed upon the pH value of the abrasives composition in accordance with the present invention. However, the pH value of the abrasives composition is preferably 5 or lower, more preferably 2.0 to 4.5, and most preferably 2.5 to 4.0. When the pH value of the abrasives composition is 5 or lower, oxidation occurs on the surface of the substrate during the abrasive processing step, which aids the mechanical abrasion of the surface, and the surface roughness of the substrate can favorably be adjusted to be very low. By way of example, in order for the pH value of the abrasives composition to be 5 or lower, a metal salt having an oxidizing group, which will be described later, an inorganic acid such as sulfuric acid or nitric acid, an organic acid, or the like, may be added to the abrasives composition.

An abrasion accelerator is present in the abrasives composition in accordance with the present invention. By way of example, as the abrasion accelerator, a metal salt containing an oxidizing group may preferably be used. The metal salt containing an oxidizing group has the effect of promoting the oxidation of the surface of the substrate during the abrasive processing step and promoting the progress of the mechanical abrasion of the surface. The various abrasion accelerators may be used alone, or two or more may be used in combination. Generally, the metal salt containing an oxidizing group may be a metal halide, a metal salt of an organic acid, or a metal salt of an oxygen containing acid.

As the oxidizing group, any oxidizing group having oxidizing effects may be used. Examples of oxidizing groups include a nitrate group, a sulfate group, a sulfite group, a persulfate group, a chloride group, a perchlorate group, a phosphate group, a phosphite group, a hypophosphite group, a pyrophosphate group, a carbonate group, a lactate group, and an oxalate group. Among the above-enumerated oxidizing groups, the nitrate group and the sulfate group are particularly preferable.

Examples of metals constituting the metal salts containing the oxidizing groups include aluminum, magnesium, nickel, and iron. Among the above-enumerated metals, aluminum and magnesium are preferable.

The content of the abrasion accelerator in the abrasives composition in accordance with the present invention is preferably 0.05% to 30% by weight, and more preferably 0.3% to 20% by weight. When the content of the abrasion accelerator in the abrasives composition is within the afore-

said range, appropriate oxidizing effects can be obtained. Therefore, the substrate can be processed efficiently to a desired low surface roughness (e.g., of less than 4Å), and the production efficiency can be increased.

The abrasives composition in accordance with the present invention can be prepared by, for example, adding the intermediate alumina particle, the abrasion accelerator, and the other components which will be described later, into water under stirring.

The content of water in the abrasives composition in accordance with the present invention is preferably 40% to 99.9% by weight, and more preferably 85% to 99.5% by weight. When the content of water in the abrasives composition falls within the aforesaid range, the substrate can be processed efficiently to a desired low surface roughness (e.g., of less than 4Å), and the production efficiency can be increased.

If necessary, components other than those described above may also be added to the abrasives composition in accordance with the present invention. Examples of such other components include a dispersing agent for the abrasive, and a dispersing agent for fine powders which occur as a result of abrasion. The content of these components in the abrasives composition is preferably 0.5% to 10% by weight.

The substrate to be abraded with the abrasives composition in accordance with the present invention is preferably a substrate for a magnetic recording medium, for example, a carbon substrate, in particular a glass-like carbon substrate. However, the type of the substrate is not limited thereto. For example, the abrasives composition in accordance with the present invention is also applicable to the abrasive processing of other substrates, e.g. a glass substrate such as a reinforced glass substrate and a glass ceramic, and an aluminum substrate.

When the abrasives composition in accordance with the present invention is used for the polishing process carried out on the substrate for a magnetic recording medium, an abraded substrate having a low surface roughness, which is necessary to satisfy the recent demand for recording information on a magnetic recording medium at high densities, can be obtained.

A preferred process for producing the substrate for a magnetic recording medium, in which the abrasive processing step is carried out with the abrasives composition in accordance with the present invention, will be described below with reference to FIGS. 1 and 2, by taking the super-polishing process of a glass-like carbon substrate as an example. FIG. 1 is a schematic front view showing a double-sided polishing machine, which may be used in a polishing step in the production of a substrate for a magnetic recording medium. FIG. 2 is a view taken along line X—X of FIG. 1.

With reference to FIGS. 1 and 2, a double-sided polishing machine 2 is provided with a base 3 and a lower lap 4, which is located on the base 3 and rotates in the direction indicated by the arrow A. A polishing pad 5 is fitted to the upper surface of the lower lap 4.

As illustrated in FIG. 2, a plurality of planetary gear-like carriers 8 are located on the upper side of the lower lap 4. Each carrier 8 is engaged with a sun gear 6, which is located at the center of the lower lap 4 and rotates in the direction indicated by the arrow B, and an internal gear 7, which is located on the outer circumference of the lower lap 4 and rotates in the direction indicated by the arrow C. Thus each carrier 8 rotates around the sun gear 6 and around its own

axis. Each carrier 8 has a plurality of holes, and glass-like carbon substrates 1 serving as work pieces are respectively set in the holes.

Also, as illustrated in FIG. 1, an upper lap 9 is located above the lower lap 4 and the carriers 8. An polishing pad (not shown) is fitted to the lower surface of the upper lap 9. The upper lap 9 is rotatably mounted on a bracket 11, which is fitted to the end of the output rod of an air cylinder 10. The upper lap 9 can be moved up and down by the air cylinder 10. When the upper lap 9 is moved down, it is engaged with grooves of a rotor 12 on the base side. The rotor 12 rotates in the direction indicated by the arrow D in FIG. 2, and the associated upper lap 9 rotates in the same direction.

The abrasives composition in accordance with the present invention is supplied from a slurry feed pipe (not shown) to the position between the upper lap 9 and the lower lap 4.

When the upper lap 9 is moved down by the air cylinder 10, the glass-like carbon substrates 1, which move together with each carrier 8, are sandwiched between the lower lap 4 and the upper lap 9. In this manner, the abrasive processing is carried out.

In general, the super-polishing process of glass-like carbon substrates may be carried out with the aforesaid double-sided polishing machine under the conditions described below.

Specifically, the processing pressure is preferably 10 to 2,000 g/cm², and more preferably 30 to 1,500 g/cm².

The processing time is preferably 2 to 120 minutes, and more preferably 2 to 30 minutes.

The hardness [JIS A(JIS K-6301)] of the abrasion pads fitted to the platens of the double-sided polishing machine is preferably 40 to 100, and more preferably 60 to 100.

The rotation speed of the lower lap of the double-sided polishing machine may vary in accordance with the size of the polishing machine. For example, as for a 9B type double-sided polishing machine manufactured by SPEED FAM CO., the rotation speed of the lower lap is preferably 10 to 100 rpm, and more preferably 10 to 60 rpm.

The supplying rate of the abrasives composition may vary in accordance with the size of the polishing machine. For example, as for the 9B type double-face polishing machine manufactured by SPEED FAM CO., the supplying rate of the abrasives composition is preferably 5 to 300 cc/min, and more preferably 10 to 150 cc/min.

When the super-polishing process is carried out on glass-like carbon substrates, i.e. the abrasive processing is carried out on the surfaces of a glass-like carbon substrate, under the conditions described above, a glass-like carbon substrates, which are ordinarily difficult to process to smooth surfaces, can be processed to a surface roughness of less than 4 Å.

The preferred process for producing the substrate for a magnetic recording medium, in which the abrasive processing step is carried out with the abrasives composition in accordance with the present invention, has been described above. However, the production process is not limited to the embodiment described above and may be applied to, for example, substrates other than the glass-like carbon substrates. In addition, the abrasives composition of the present invention is advantageous for the production of substrates other than a substrate for a magnetic recording medium, for example, a silicon wafer and various lenses which require a low surface roughness.

In the present invention, the magnetic recording medium can be obtained by using the glass-like carbon substrate which has been obtained in the manner described above and

has a surface roughness of less than 4 Å, and forming at least a magnetic layer and a protective layer, in this order, on the substrate. The surface roughness of the magnetic recording medium reflects the surface roughness of the glass-like carbon substrate (i.e., less than 4 Å) and can be reduced to a very small value. Therefore, the magnetic recording medium obtained in accordance with the present invention is advantageous over the magnetic recording medium which is provided with a glass-like carbon substrate (having a surface roughness of approximately 10 Å) obtained by conventional abrasion techniques, in that the glide height of the magnetic head can be reduced to a very small value, and in that information can be recorded at high densities.

In the present invention, the surface roughness (center line mean roughness Ra) may be measured with an atomic force microscope.

In the magnetic recording medium of the present invention, the magnetic layer may be formed directly on the glass-like carbon substrate. However, it is preferred that at least one under layer is formed between the glass-like carbon substrate and the magnetic layer, as described in Examples 4 to 6. The preferable material of the under layer is a nonmagnetic, highly crystalline metal. Examples of preferable materials for the under layer include Ti, Cr, W, Si, Al, and alloys of these metals.

Also, in the magnetic recording medium, if necessary, a layer having an uneven surface may be formed between the glass-like carbon substrate and the magnetic layer. The degree of unevenness of the layer is preferably as low as possible from the viewpoint of the reduction in the glide height of the magnetic head, provided that the magnetic head does not stick to the surface of the magnetic recording medium. For example, as for a magnetic disk drive in which the contact start and stop (CSS) system is employed, the layer having an uneven surface is preferably located only in the CSS region (i.e., head landing zone). As for a magnetic disk drive in which the magnetic head does not come into contact with the magnetic recording medium, it is preferable that the layer having an uneven surface is not formed. The layer having an uneven surface may be formed with a technique for carrying out tape texturing only at a prescribed area on the surface of the glass-like carbon substrate which has been obtained from the abrasive processing step using the aforesaid abrasives composition, a technique for texturing with the spraying of fine particles, a technique for texturing with irradiation of a laser beam, or a technique for sputtering Al, Si, or an Al-M alloy, where M represents a metal having the capability to form a carbide.

As the material of the magnetic layer of the magnetic recording medium, Co-alloys containing Co as a principal constituent are preferable. The Co-alloys comprising Cr (CoCr alloys) are more preferable, and the Co-alloys comprising Cr and Pt (CoCrPt alloys) are particularly preferable. Specifically, CoCrPtB, CoCrPtTa, or the like, are preferable.

As the material of the protective layer of the magnetic recording medium, carbons, particularly amorphous carbon and diamond-like carbon, are preferable.

In the magnetic recording medium, if necessary, a lubricant layer may be provided on the protective layer. As the lubricant, for example, a perfluoroalkyl ether lubricant is preferable.

Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

EXAMPLES 1, 2, 3 AND COMPARATIVE EXAMPLES 1, 2, 3

An abrasives composition, as a slurry, was prepared by mixing 1% by weight of the abrasive listed in Table 1, 1% by weight of aluminum nitrate, serving as an abrasion accelerator (in Comparative Example 2, aluminum nitrate was not added), and the balance of water, and stirring the resulting mixture. The abrasives composition obtained had a pH value listed in Table 1.

Thereafter, a glass-like carbon substrate, which had a diameter of 2.5 inches and the surface roughness of approximately 12 Å with a polishing process, was set in the double-sided polishing machine. The surface of the glass-like carbon substrate was thus subjected to a super-polishing process with the prepared abrasives composition. The abrasive processing with the double-sided polishing machine was carried out under the conditions shown below.

Setting conditions of double-sided polishing machine
Double-sided polishing machine used: 9B type double-sided polishing machine manufactured by SPEED FAM CO.

Processing pressure: 150 g/cm²

Processing time: 30 min

Hardness of polishing pad: 90

Rotation speed of lower lap: 40 rpm

Supplying rate of abrasives composition: 50 cc/min

The surface roughness Ra and the number of defects on the surface of glass-like carbon substrate, obtained from the super-polishing process, were measured with the methods described below. The results are shown in Table 1.

Surface roughness Ra

The surface roughness Ra of 10×10 μm surface area was measured by using an atomic force microscope (AFM) image (NANOSCOPE III manufactured by DIGITAL INSTRUMENTAL CO.).

Number of defects

The surface of the substrate was observed by using an optical microscope (×200), and the number of defects, having a size of 0.5 μm or larger on the entire surface of the substrate, was counted.

EXAMPLES 4, 5, 6 AND COMPARATIVE EXAMPLES 4, 5, 6

With a sputtering process, a Ti layer (first under layer), a Cr layer (second under layer), a Co₇₆Cr₁₂Pt₈B₄ layer (magnetic layer), and an amorphous carbon layer (protective layer) were successively formed to predetermined thicknesses on each of the glass-like carbon substrates obtained in Examples 1, 2, 3 and Comparative Examples 1, 2, 3. Further, a lubricant layer was formed to a predetermined thickness on the protective layer by the dip-coating of FOMBLIN Z-03 manufactured by AUGIMONT CO. In this manner, a magnetic disk was obtained. As for the obtained magnetic disk, a glide height test (GHT) was carried out under the conditions shown below. The results are shown in Table 2.

GHT

Magnetic Head: MG150T, 50% slider head manufactured by PROQUIP CO.

Passage rate: at a glide height of 1.0 μ inch

Evaluation scale:

Passage rate of 95% to 100%; Very good

Passage rate of 70% to less than 95%; Good

Passage rate of less than 70%; Poor

TABLE 1

	Type of Alumina	Particle Size* of Alumina (nm)	pH of Abrasives Composition	Aluminum Nitrate (wt %)	Surface Roughness (Å)	Number of Defects (pieces)
Examples	1 γ -Al ₂ O ₃	20	3.8	1	3.2	0
	2 γ -Al ₂ O ₃	40	3.8	1	3.9	0
	3 θ -Al ₂ O ₃	30	3.8	1	3.9	0
Comparative Examples	1 α -Al ₂ O ₃	1000	3.8	1	12.1	0
	2 γ -Al ₂ O ₃	40	7.2	0	15.0	>500
	3 γ -Al ₂ O ₃	45	3.8	1	5.3	120

*Mean particle size of primary particles

TABLE 2

		GHT
Examples	4	Very Good
	5	Very Good
	6	Very Good
Comparative Examples	4	Poor
	5	Poor
	6	Good

As is clear from the results shown in Table 1, when the super-polishing process was carried out on the glass-like carbon substrates using the abrasive compositions in accordance with the present invention (Examples 1, 2 and 3), no defect occurred on the surface of the abraded substrates, and the surface roughness of the abraded substrates could be reduced to a very small value (less than 4 Å). On the other hand, when α -alumina particles were used as the abrasive (Comparative Example 1), though no defect occurred, the low surface roughness obtainable with the abrasive composition in accordance with the present invention could not be obtained. Also, when the abrasive processing was carried out with an abrasives composition containing no abrasion accelerator (Comparative Example 2), many defects occurred on the surface of the abraded substrate, and the low surface roughness obtainable with the abrasive compositions in accordance with the present invention could not be obtained. Further, in cases where the abrasive processing was carried out with the abrasives composition containing the abrasive having a mean particle size larger than 40 nm (Comparative Example 3), defects occurred on the surface of the abraded substrate, and the low surface roughness obtainable with the abrasive compositions in accordance with the present invention could not be obtained.

Also, as is clear from the results shown in Table 2, the magnetic disks (Examples 4, 5 and 6) which use the glass-like carbon substrates (obtained in Examples 1, 2 and 3) subjected to the super-polishing process using the abrasive compositions in accordance with the present invention, had a low substrate surface roughness and exhibited good GHT results. On the other hand, the magnetic disks (Comparative Examples 4, 5 and 6) which use the substrates obtained in Comparative Examples 1, 2 and 3, exhibited GHT results inferior to those obtained with the magnetic disks of Examples 4, 5 and 6, because the magnetic disks in Comparative Examples 4, 5 and 6 do not use substrates having a surface roughness as low as obtained in Examples 1, 2 and 3.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teaching. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described therein.

15 The priority documents of the present application, Japanese Patent Applications No. 7-292567 and No. 8-71577, filed on Nov. 10, 1995 and Mar. 27, 1996, respectively, are hereby incorporated by reference.

20 What is claimed as new and is desired to be secured by Letters Patent of the United States is:

1. An abrasives composition, comprising:

- (i) one or more abrasives,
- (ii) one or more abrasion accelerators, and
- (iii) water,

wherein said abrasives consist essentially of intermediate alumina particles having a mean particle size of primary particles of 40 nm or less wherein said intermediate alumina particles comprise an abrasive effective amount of at least one member selected from the group consisting of γ -alumina and θ -alumina.

2. The abrasives composition of claim 1, wherein said abrasives composition has a pH of 5 or less.

3. The abrasives composition of claim 1, wherein said abrasion accelerator comprises at least one metal salt containing an oxidizing group.

4. The abrasives composition of claim 1, wherein said intermediate alumina particles have a mean particle size of primary particles of 10 to 40 nm.

5. The abrasives composition of claim 1, comprising: 40 to 99.9% by weight of said water,

0.05 to 30% by weight of said abrasion accelerator, and 0.05 to 30% by weight of said intermediate alumina particles.

6. The composition according to claim 1, wherein said intermediate alumina particles comprise γ -alumina.

7. An abrasives composition, prepared by mixing 40 to 99.9% by weight of water,

0.05 to 30% by weight of at least one abrasion accelerator, and

0.05 to 30% by weight of, one or more abrasives, wherein said abrasives consist essentially of intermediate alumina particles having a mean particle size of primary particles of 40 nm or less and comprise an abrasive effective amount of at least one member selected from the group consisting of γ -alumina and θ -alumina.

8. The abrasives composition of claim 7, wherein said intermediate alumina particle comprises γ -alumina.

9. A process for producing a substrate, comprising: abrading a surface of said substrate with an abrasives composition.

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wherein said abrasives composition comprises

- (i) one or more abrasives,
- (ii) one or more abrasion accelerators, and
- (iii) water, and

said abrasives consist essentially of intermediate alumina particles having a mean particle size of primary particles of 40 nm or less and comprise an abrasive effective amount of at least one member selected from the group consisting of γ -alumina and θ -alumina.

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10. The process of claim 9, wherein said abrasives composition has a pH of at most 5.

11. The process of claim 9, wherein said abrading is carried out until said surface of said substrate has a surface roughness Ra of less than 4Å.

12. The process of claim 9, wherein said substrate comprises amorphous carbon.

13. The process as claimed in claim 9, wherein said intermediate alumina particles comprise γ -alumina.

* * * * *



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United States Patent [19]

Miyashita et al.

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[54] POLISHING SLURRY

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[*] Notice: This patent issued on a continued prosecution application filed under 37 CFR 1.53(d), and is subject to the twenty year patent term provisions of 35 U.S.C. 154(a)(2).

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[52] U.S. Cl. **106/3; 252/79.1; 252/79.2;**

252/79.3; 430/692; 430/693

[58] Field of Search 252/79.1, 79.2,

252/79.3; 106/3; 156/645.1, 345 LP; 438/692,
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U.S. PATENT DOCUMENTS

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Garrett & Dunner, L.L.P.

[57] ABSTRACT

A polishing slurry for use in chemical mechanical polishing is disclosed. The polishing slurry contains a solvent and polishing particles dispersed in this solvent. The polishing particles are selected from silicon nitride, silicon carbide, and graphite. The primary particle size of the polishing particles dispersed in the solvent is appropriately 0.01 to 1000 nm. When the polishing particles are colloiddally dispersed in the solvent, the secondary particle size of the polishing particles is appropriately 60 to 300 nm.

15 Claims, 10 Drawing Sheets

POLISHING PARTICLES	POLISHING RATE (nm / min)	SELECTION RATE (SiO ₂ /Si ₃ N ₄)	PLANARITY (%)
(I) CeO	500 ~ 800	1 ~ 3	15 ~ 20
(II) Fumed SiO ₂	100 ~ 110	2 ~ 3	15 ~ 20
(III) Al ₂ O ₃	150 ~ 200	1	10
(IV) Si ₃ N ₄	700 ~ 1000	10 ~ 20	2 ~ 5

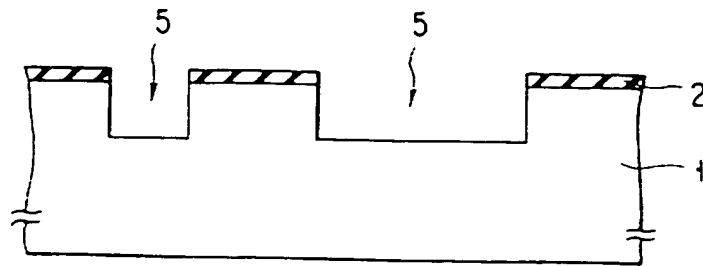


FIG. 1A

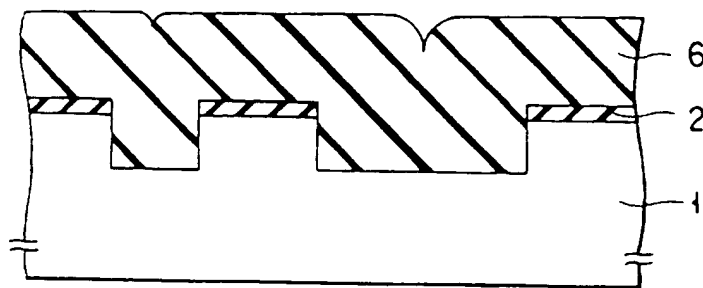


FIG. 1B

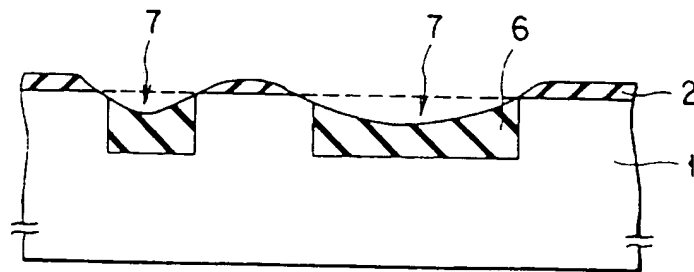


FIG. 1C

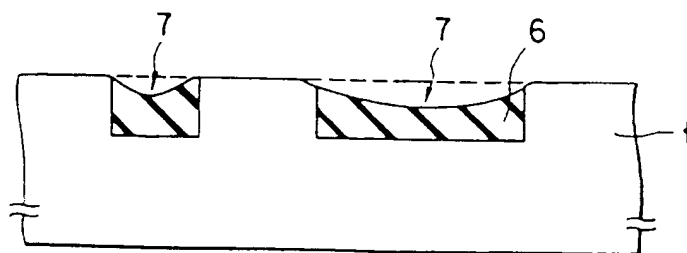


FIG. 1D

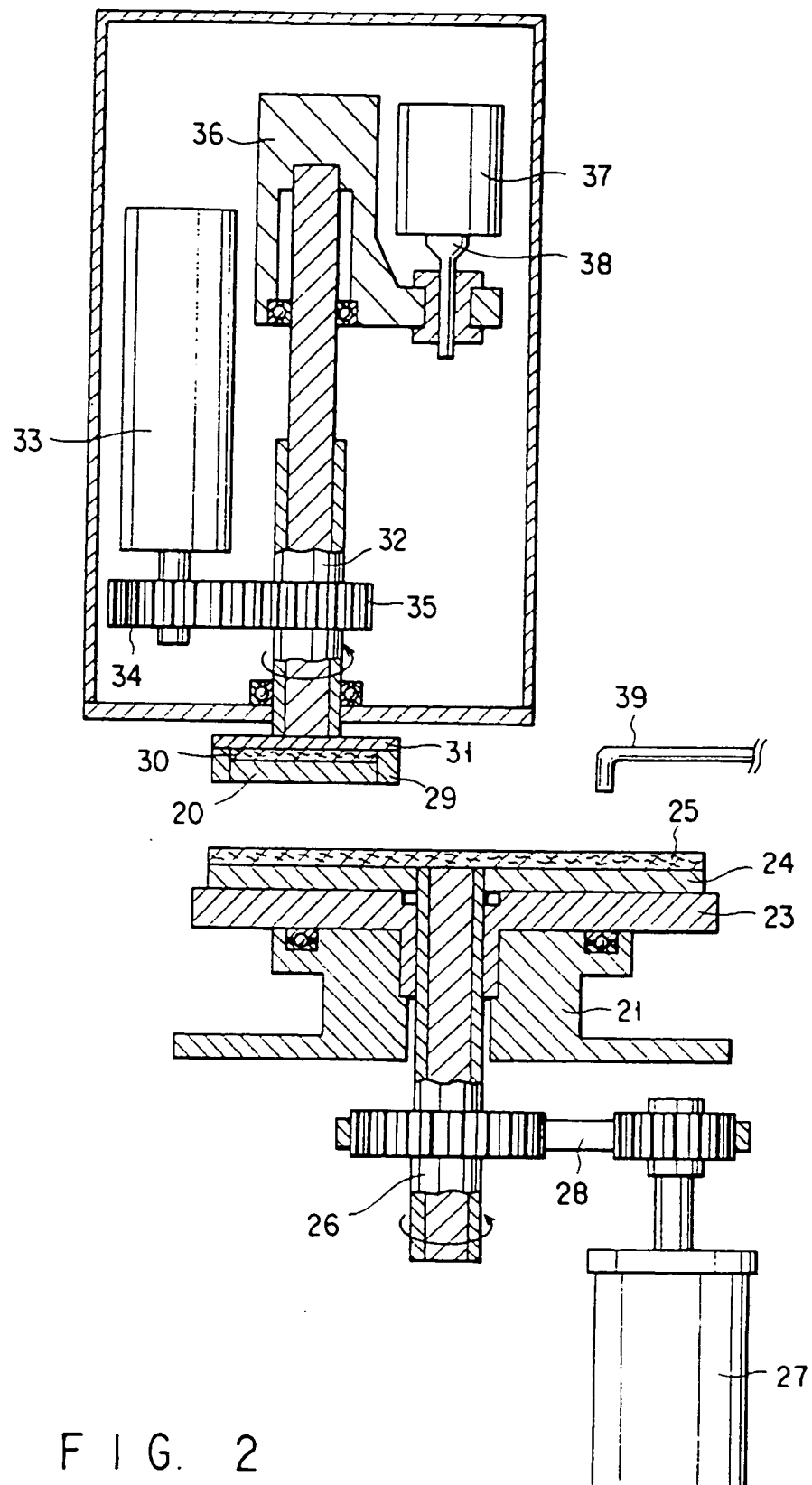


FIG. 3A

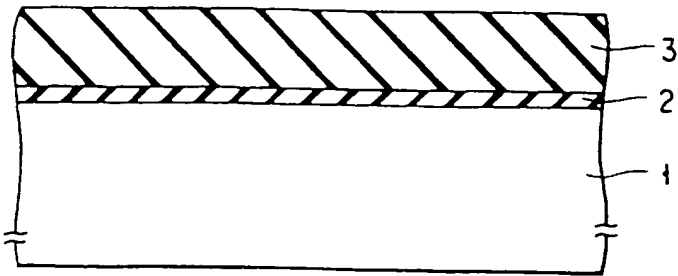


FIG. 3B

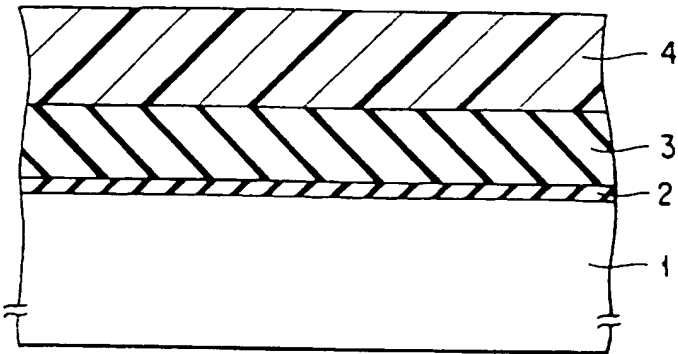


FIG. 3C

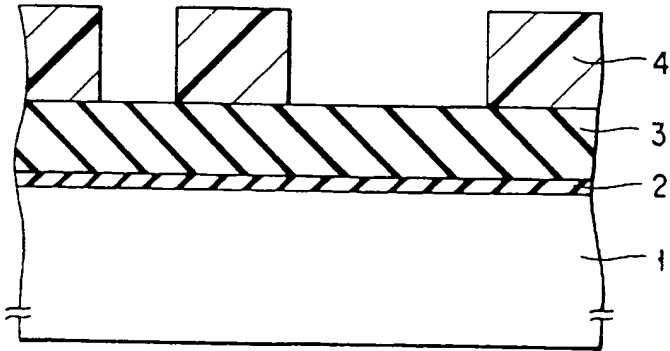


FIG. 3D

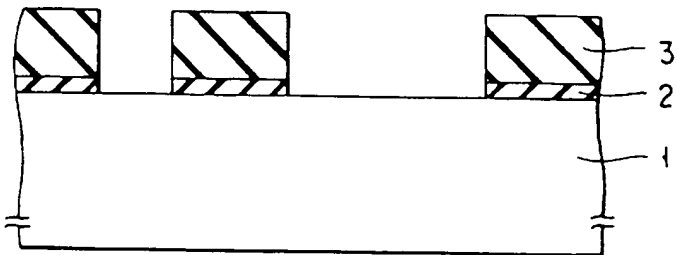


FIG. 3E

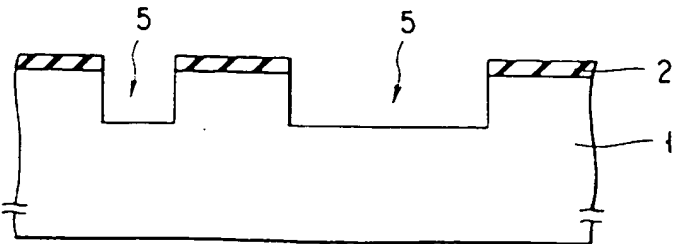


FIG. 3F

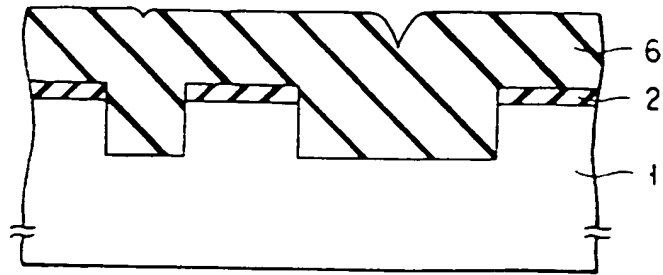


FIG. 3G

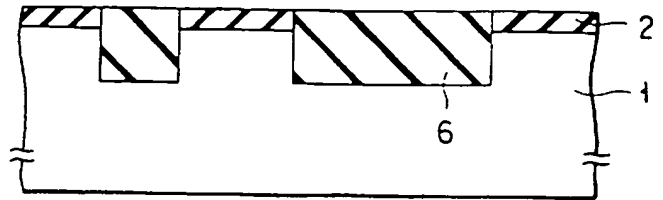


FIG. 3H

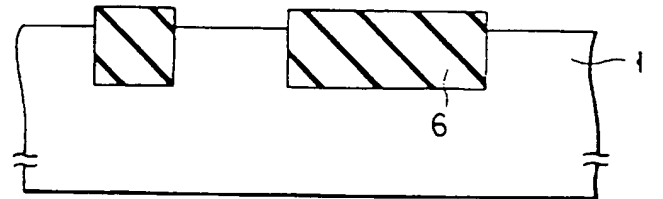
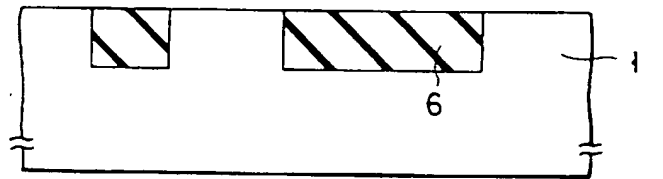


FIG. 3I



POLISHING PARTICLES	POLISHING RATE (nm / min)	SELECTION RATE (SiO ₂ /Si ₃ N ₄)	PLANARITY (%)
(I) CeO	500 ~ 800	1 ~ 3	15 ~ 20
(II) Fumed SiO ₂	100 ~ 110	2 ~ 3	15 ~ 20
(III) Al ₂ O ₃	150 ~ 200	1	10
(IV) Si ₃ N ₄	700 ~ 1000	10 ~ 20	2 ~ 5

FIG. 4

FIG. 5A

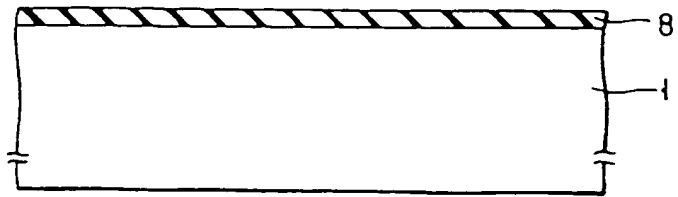


FIG. 5B

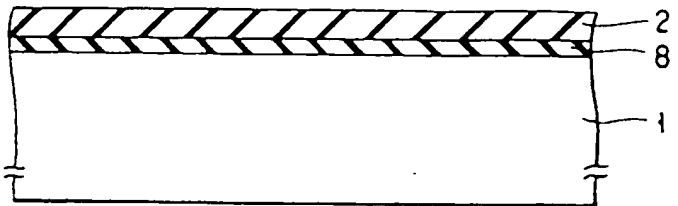


FIG. 5C

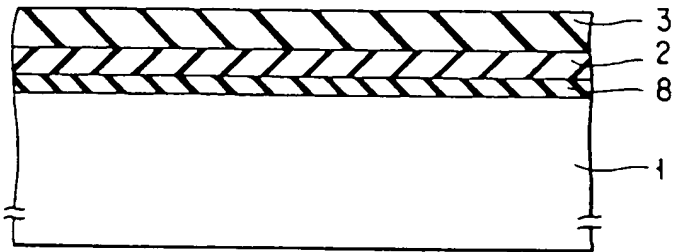


FIG. 5D

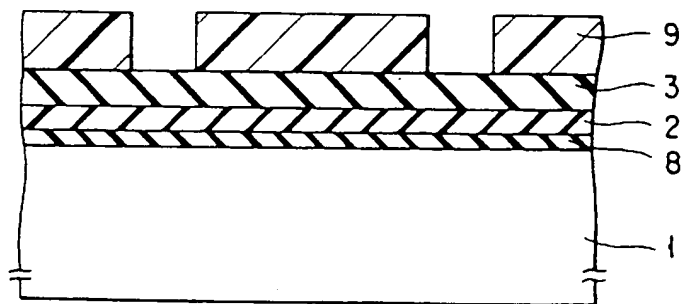


FIG. 5E

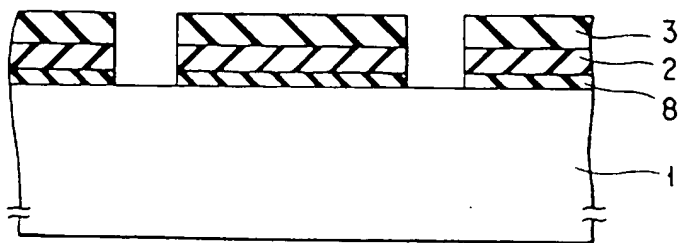


FIG. 5F

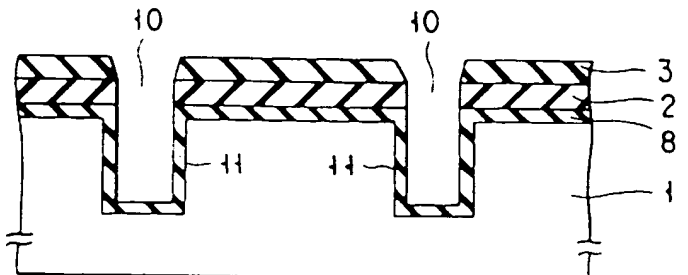


FIG. 5G

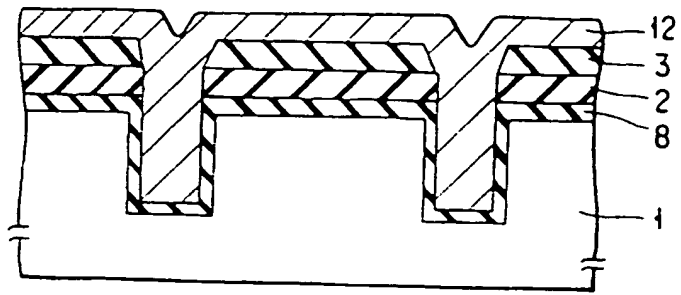


FIG. 5H

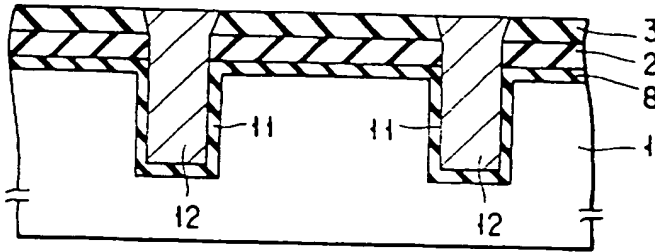


FIG. 5I

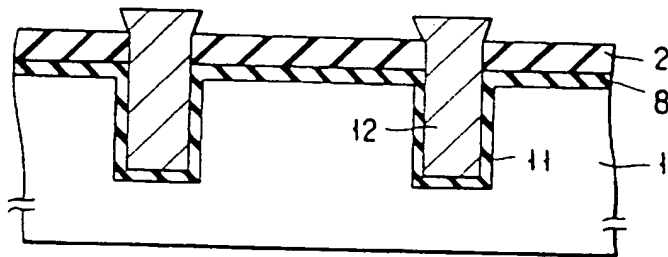


FIG. 5J

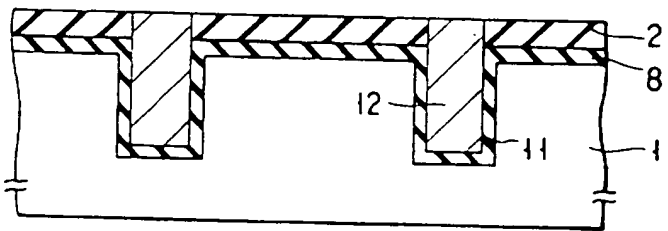


FIG. 5K

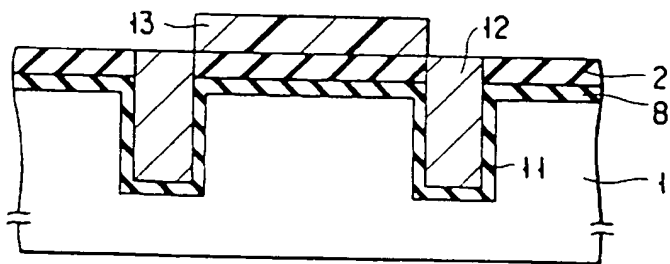


FIG. 5L

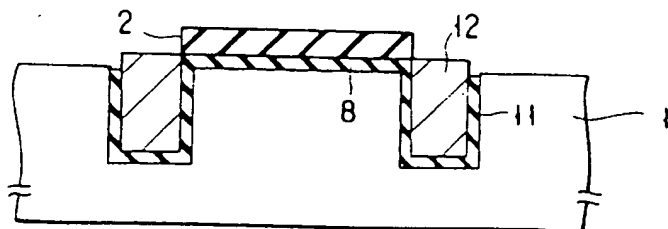


FIG. 5M

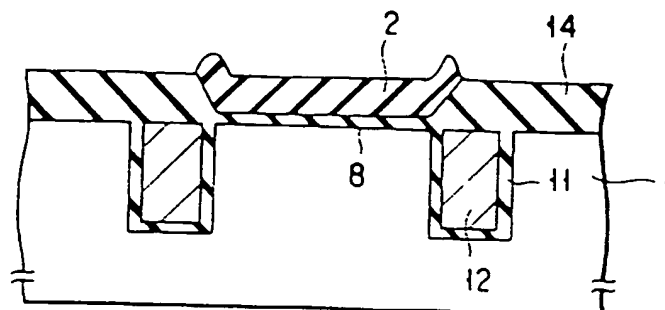


FIG. 6A

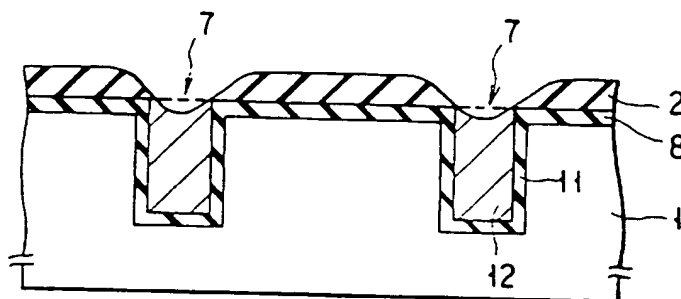


FIG. 6B

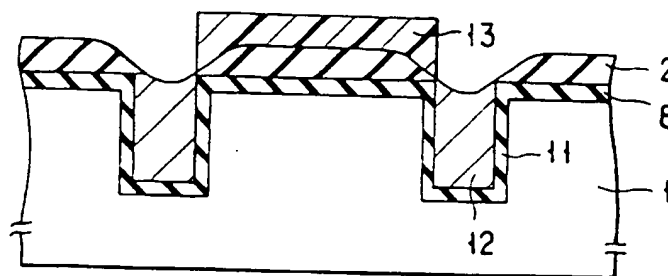


FIG. 6C

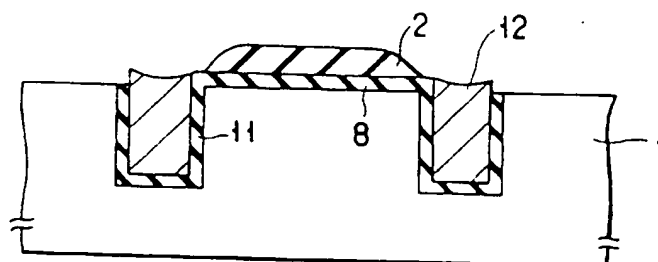


FIG. 6D

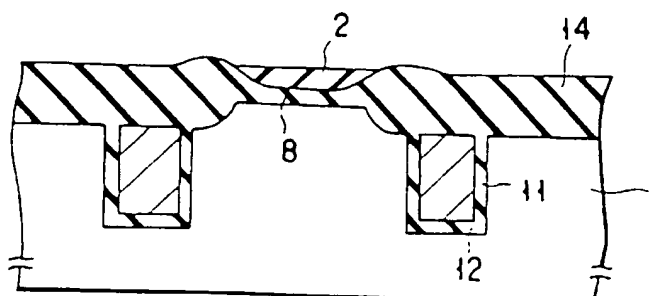


FIG. 7A

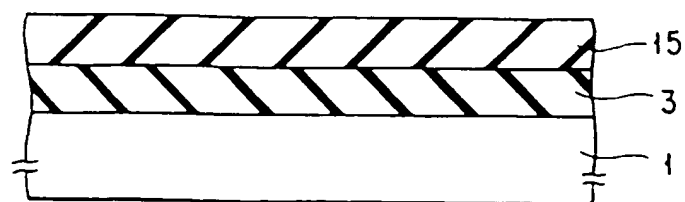


FIG. 7B

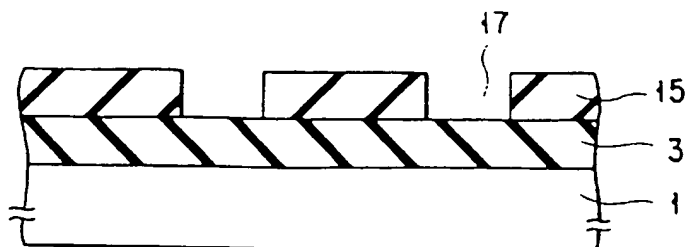


FIG. 7C

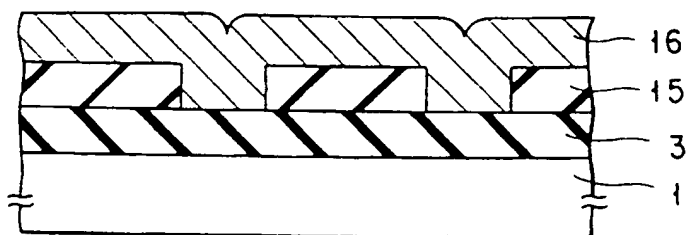


FIG. 7D

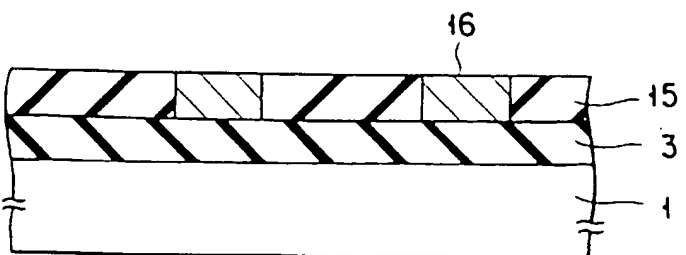
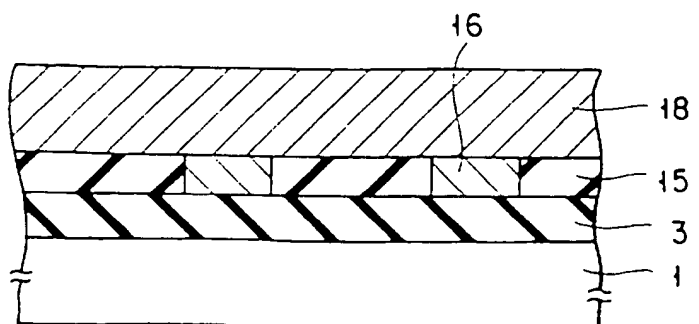


FIG. 7E



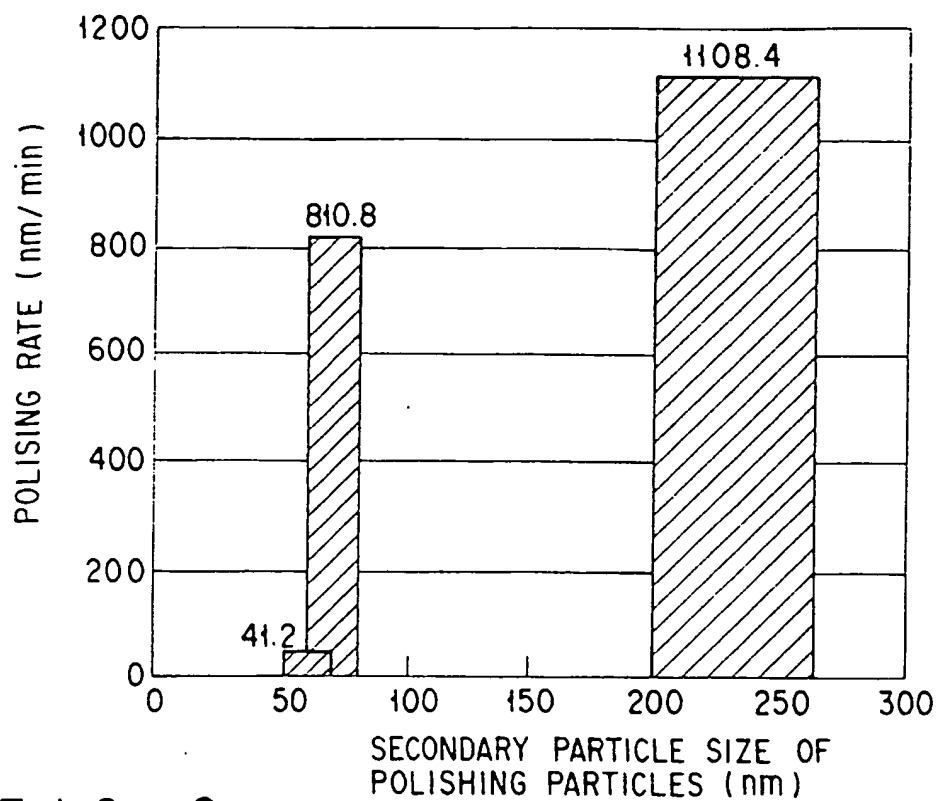


FIG. 8

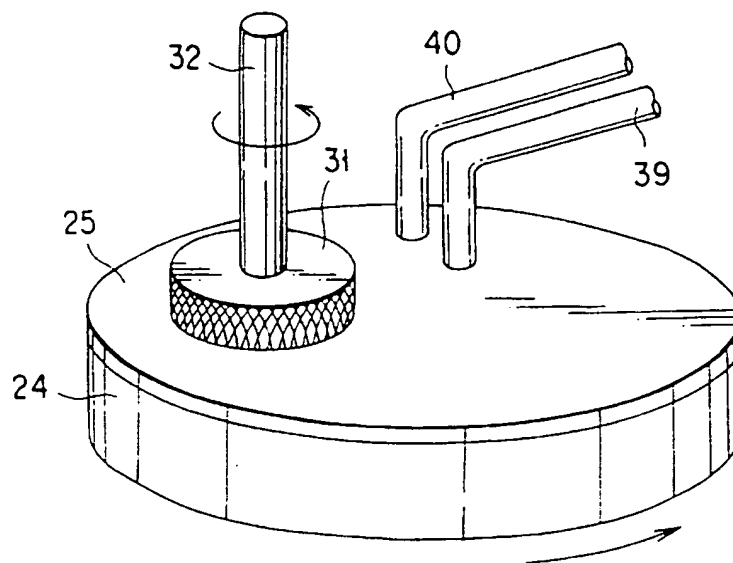


FIG. 9

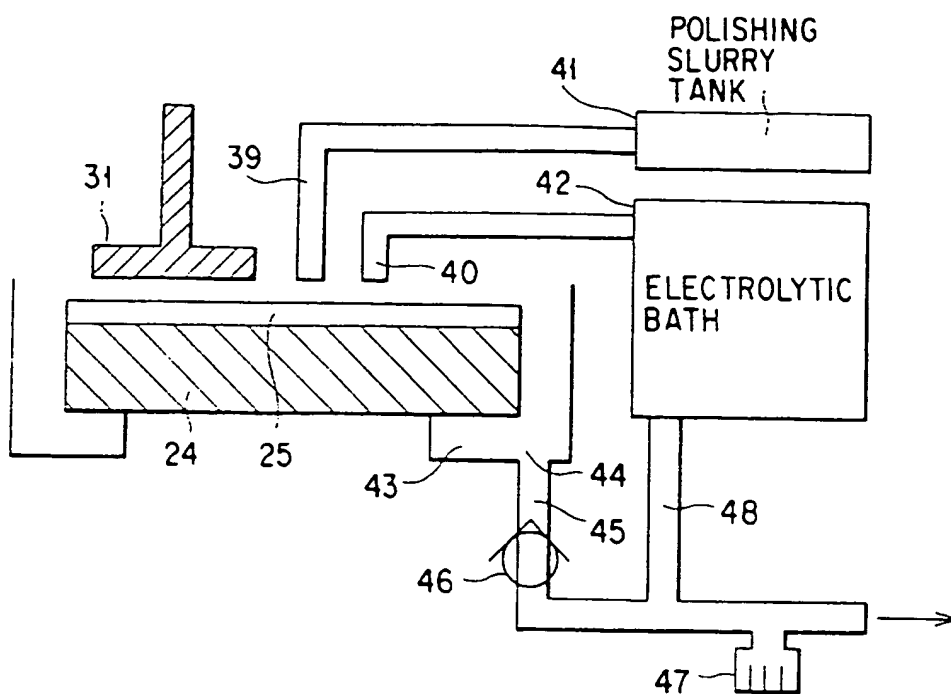


FIG. 10

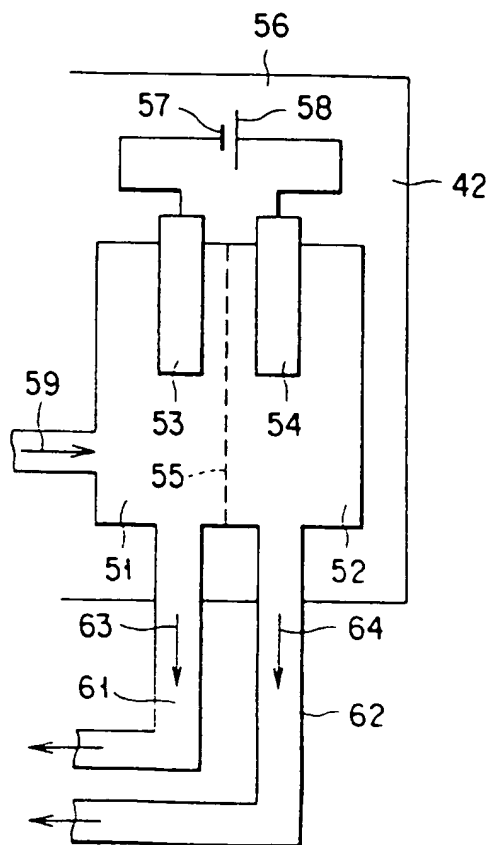


FIG. 11

POLISHING SLURRY

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a polishing slurry used in the fabrication of semiconductor devices and, more particularly, to a polishing slurry used in CMP (Chemical Mechanical Polishing).

2. Description of the Related Art

Semiconductor devices such as ICs and LSIs are typically fabricated through the following steps: an integrated circuit designing step of designing integrated circuits; a photomask formation step of forming a photomask used in a lithography step; a wafer manufacturing step of manufacturing wafers having a predetermined thickness from a single-crystal ingot; a wafer processing step of forming a plurality of integrated circuits on each wafer; a dicing step of dicing each of the integrated circuits formed on the wafer into the shape of a semiconductor chip; an assembly step of packaging the diced semiconductor chips; and a testing step of testing the packaged semiconductor chips. Of these steps, the wafer processing step is most important. The wafer processing step is further subdivided into a thin film deposition step of depositing a thin film, a lithography step of exposing/developing a photoresist, an etching step of etching a wafer or the deposited thin film, and an ion implantation step of implanting an impurity ion into the wafer or the deposited thin film. These steps are done by using semiconductor fabrication apparatuses dedicated to the respective steps.

The techniques used in the etching step are roughly classified into two categories.

One is selective etching in which the target surface is masked using a photoresist and only selected portions are etched. This etching is used in the patterning of interconnections and the formation of contact holes.

The other is etch back by which a whole wafer is evenly etched. This etch back is performed to planarize the wafer surface roughened by interconnections or planarize the wafer surface after trenches or recesses are buried with a thin film. As a method of etch back, a method of performing RIE (Reactive Ion Etching) on the wafer surface after recesses on the wafer surface are buried with a photoresist is used most often (this method will be referred to as etch back-RIE hereinafter). Unfortunately, this etch back-RIE has some disadvantages that the method requires a step of coating the target surface with a photoresist, damages easily remain on the wafer surface after etch back, a dangerous etching gas is used in an RIE apparatus, and the global planarization of an entire wafer is rather low due to variations of the etching rate on the wafer surface.

In consideration of these drawbacks, CMP (Chemical Mechanical Polishing) is recently beginning to be studied in place of etch back-RIE.

In CMP, the surface to be polished of a wafer is pressed against a polishing pad adhered to a polishing disc, and the wafer and the polishing disc are rotated while a polishing agent is supplied to the polishing pad, thereby polishing the surface to be polished. The polishing agent used in CMP is a liquid prepared by dispersing polishing particles which mechanically polish the surface to be polished in a polishing solution which chemically etches the surface. This liquid polishing agent has a function of setting the surface to be polished in an active state in which the surface is readily chemically polished, thereby assisting the mechanical pol-

ishing by the polishing particles. This liquid polishing agent is called a slurry.

CMP can alleviate some problems of etch back-RIE. However, although CMP can achieve high global planarization, the local planarization obtained by CMP is found to be low in fine portions of a semiconductor device structure. When the wafer surface planarized by using CMP is observed, fine micron-order dish-like recesses called "dishing" are found in fine portions of a semiconductor device structure, particularly in portions made from different substances on the wafer surface.

A typical condition in which "dishing" occurs will be described below with reference to FIGS. 1A to 1D.

FIGS. 1A to 1D are sectional views showing trench isolation steps in order.

FIG. 1A shows the state in which trenches 5 are formed in a silicon substrate 1. A polishing stopper film 2 is formed on the surface of the silicon substrate 1 except the portions in which the trenches 5 are formed. This stopper film 2 is a nitride film (Si_3N_4).

Subsequently, as shown in FIG. 1B, silicon dioxide (SiO_2) is deposited inside the trenches 5 and on the stopper film 2, forming an oxide film 6. The trenches 5 are buried with the oxide film 6.

In FIG. 1C, CMP is performed for the oxide film 6. As a consequence, the surface of the oxide film 6 dishes to form "dishing" 7.

In FIG. 1D, the stopper film 2 is removed.

In trench isolation in which the "dishing" 7 is formed as shown in FIGS. 1C and 1D, a conductive thin film may remain in the "dishing" 7. If a conductive thin film remains in the "dishing" 7, this film can bring about defective insulation in the future. This influences the reliability of the semiconductor device.

SUMMARY OF THE INVENTION

An important subject is to realize CMP capable of preventing "dishing".

To achieve the above subject, the inventors of this application have focused attention on polishing particles contained in a polishing slurry.

Presently, the polishing particles contained in a polishing slurry are cerium oxide particles or silica particles.

A polishing slurry (to be referred to as a polishing slurry (I) hereinafter) containing cerium oxide particles has a high polishing rate of about 0.5 to 1.0 $\mu\text{m}/\text{min}$ for an oxide film (SiO_2) but has a low selection rate ($\text{SiO}_2/\text{Si}_3\text{N}_4$) of about 2 with respect to a nitride film (Si_3N_4) as a stopper film. Even if polysilicon (Si) is used as a stopper film, the selection rate (SiO_2/Si) is about 1 to 2.

As described above, the polishing slurry (I) has a high polishing rate and a lower selection rate with respect to a stopper film. Accordingly, the polishing slurry (I) readily causes overpolishing and this may scrape off a stopper film and enlarge "dishing".

In contrast, a polishing slurry (to be referred to as a polishing slurry (II) hereinafter) containing silica particles has a polishing rate of about 0.1 to 0.15 $\mu\text{m}/\text{min}$ for an oxide film (SiO_2) which is lower than that of the polishing slurry (I). Also, when a stopper film is a nitride film (Si_3N_4), the selection rate ($\text{SiO}_2/\text{Si}_3\text{N}_4$) is about 2. Even if polysilicon (Si) is used as a stopper film, the selection rate (SiO_2/Si) is about 1.

As described above, even the polishing slurry (II) has a low selection rate with respect to a stopper film and therefore

A wafer carrier 31 is arranged in a position opposite to the polishing pad 25. A retainer ring 29 is attached to the wafer carrier 31. An adsorption pad 30 is attached to a hole formed in the retainer ring 29. The wafer 20 is adsorbed by the adsorption pad 30 by vacuum or water and carried by the wafer carrier 31. The central portion of the wafer carrier 31 is connected to a driving shaft 32 for rotating the carrier 31. The shaft 32 is rotated by a motor 33 via gears 34 and 35. The shaft 32 is attached to a driving base 36 which is attached to a piston 38 of a cylinder 37. The driving base 36 moves vertically when the piston 38 moves vertically.

To polish the wafer 20, the wafer carrier 31 carrying the wafer 20 and the polishing pad 24 are rotated. A polishing slurry is supplied to the polishing pad 25 through a polishing slurry supply nozzle 39. A down force is applied to the wafer carrier 31 by the piston 38, thereby pushing the wafer 20 against the polishing pad 25 by a predetermined pressure. The wafer 20 is polished by maintaining this state for a time required for polishing.

A method of fabricating a semiconductor device using CMP according to the present invention will be described below.

Trench isolation steps will be described first as the first embodiment. Trench isolation is accomplished by burying trenches formed in a wafer (to be referred to as a silicon substrate hereinafter) with a CVD-oxide film (CVD-SiO₂) and planarizing the CVD-oxide film by CMP.

FIGS. 3A to 3I are sectional views showing the trench isolation steps in order.

As shown in FIG. 3A, silicon nitride (Si₃N₄) is deposited on a silicon substrate 1 to form a 70-nm thick nitride film 2. This nitride film 2 serves as a polishing stopper film. Silicon dioxide (SiO₂) is deposited on the nitride film 2 to form a CVD-oxide film 3. This CVD-oxide film 3 serves as a mask when trenches are formed.

In FIG. 3B, the CVD-oxide film 3 is coated with a photoresist to form a photoresist layer 4.

In FIG. 3C, windows corresponding to a trench formation pattern are formed in the photoresist layer 4 by photolithography.

In FIG. 3D, the CVD-oxide film 3 and the nitride film 2 are etched by RIE by using the photoresist layer 4 as a mask. Thereafter, the photoresist layer 4 is removed.

In FIG. 3E, the CVD-oxide film 3 and the silicon substrate 1 are etched by RIE. As a consequence, trenches 5 are formed in the silicon substrate 1 due to the difference between the etching rates of the CVD-oxide film 3 and the silicon substrate 1. Subsequently, a damage layer formed by RIE on the surface in the trenches 5 to which the silicon substrate 1 is exposed and reaction products formed simultaneously with RIE are removed. This is done by wet processing (wet etching).

In FIG. 3F, silicon dioxide (SiO₂) is deposited on the structure shown in FIG. 3E to form a CVD-oxide film 6. This CVD-oxide film 6 buries the trenches 5 and at the same time covers the surface of the silicon substrate 1 on which the trenches 5 are formed.

In FIG. 3G, CMP is performed by the polishing apparatus shown in FIG. 2 by using the CVD-oxide film 6 and the nitride film 2 as stopper films, thereby planarizing the surface of the structure shown in FIG. 3F.

In this CMP step, a novel polishing slurry according to the present invention is used. One example of the polishing slurry according to the present invention is prepared by dispersing silicon nitride particles as polishing particles in

nitric acid as a solvent. The polishing particles act on the CVD-oxide film 6 and mechanically polish the CVD-oxide film 6. The particle size of the silicon nitride particles themselves, i.e., the particle size of primary particles is preferably 0.01 to 1000 nm. A particle size exceeding 1000 nm is unpreferable because the mechanical polishing properties become too strong and the chemical polishing properties become extremely weak. On the other hand, if the particle size is smaller than 0.01 nm, the mechanical polishing properties become weak to make well-balanced polishing impossible. The particle size of the primary particles is particularly preferably 10 to 40 nm. If the particle size of the primary particles is 10 to 40 nm, well-balanced polishing is possible.

The silicon nitride particles can also be colloiddally dispersed in a solvent. When the silicon nitride particles are colloiddally dispersed in a solvent, the silicon nitride particles are readily evenly dispersed in the solvent. The particle size of the colloiddal silicon nitride particles, i.e., the particle size of secondary particles is preferably 60 to 300 nm, and particularly preferably 60 to 100 nm. The particle size of the secondary particles can be measured by using a centrifugal precipitation method capable of measuring particle sizes of 0.01 μm or more.

To improve the dispersibility of polishing particles, it is also possible to further mix a dispersant such as a surfactant in a polishing slurry, in addition to colloiddally dispersing the polishing particles in a solvent.

The viscosity of the polishing slurry is preferably 1 to 10 cp. If the viscosity is low, it becomes difficult to evenly disperse silicon nitride particles, i.e., polishing particles, in a solvent. When polishing particles are evenly dispersed in a solvent, the planarity of the polishing surface can be easily improved. If the viscosity is too high, the mechanical polishing properties become strong. When the mechanical polishing properties become too strong, the warpage of a wafer or the uniformity of the thickness of a deposited film has a large effect on the planarity after CMP.

The polishing temperature is preferably 20° to 70° C. This is so because if the temperature is too high, the chemical action becomes too strong.

In this first embodiment, the polishing conditions are that the rotating speed of the polishing disc 24 is 100 rpm, the rotating speed of the wafer carrier 31 is 100 rpm, the down force applied to the wafer carrier 31 is 400 g/cm², and the temperature of the polishing disc 24 is 25° to 30° C. The polishing slurry used consists of nitric acid as a solvent and silicon nitride particles as polishing particles and has a viscosity of 2 cp. This polishing slurry was supplied to the polishing pad at a flow rate of 300 cc/min to perform CMP on a 6" wafer (silicon substrate 1).

FIG. 3G shows the section after the polishing.

As shown in FIG. 3G, when the CVD-oxide film 6 is subjected to CMP by using the polishing slurry containing the silicon nitride particles, a processed shape having a small "dishing" and a high local planarization is obtained.

Subsequently, the nitride film 2 is etched away as shown in FIG. 3H.

In FIG. 3I, finish polishing is so performed that the surface of the silicon substrate 1 is flush with the surface of the CVD-oxide film 6. This completes trench isolation having a good processed shape with almost no "dishing" on the silicon substrate 1 and the CVD-oxide film 6 buried in the trenches 5.

FIG. 4 shows the results of experiments comparing the polishing rates, the selection rates, and the planarities of the

silica particles as polishing particles in nitric acid as a solvent. Consequently, dishing 7 is formed on the exposed surface of the polysilicon film 12. Also, the edges of the nitride film 2 are scraped off and abraded.

FIG. 6B corresponds to the step shown in FIG. 5K.

FIG. 6C corresponds to the step shown in FIG. 5L.

FIG. 6D corresponds to the step shown in FIG. 5M.

As shown in FIG. 6D, the exposed surface of a silicon substrate 1 and the surface of the polysilicon film 12 are thermally oxidized by using the nitride film 2 as an oxidation barrier film, thereby forming a field oxide film (SiO_2) 14 on the surface of the structure shown in FIG. 6C. Since the edges of the nitride film 2 are largely abraded, a bird's beak largely extends in the interface between the nitride film 2 and the silicon substrate 1. This is because the abraded edges of the nitride film 2 easily warp. The bird's beak extending toward the element region reduces the area of the element region. In a certain MOSFET, the width of the element region determines the gate width of the MOSFET. In a MOSFET of this sort, the gate width is narrowed by narrowing of the width of the element region. The gate width of a MOSFET determines the drivability of the MOSFET. Accordingly, if the gate width greatly deviates from the design value, the characteristics of the semiconductor device are affected.

In contrast, in the fabrication method according to the second embodiment, the edges of the nitride film 2 are abraded little and hence do not easily warp. Accordingly, the bird's beak does not easily extend and the gate width does not largely deviate from the design value. Consequently, the characteristics of the semiconductor device are not easily affected.

Also, in the fabrication method according to the second embodiment, the conversion difference between the LOCOS patterns is small because the bird's beak is small. Accordingly, the method is suitable for fine element region patterns.

As the third embodiment, steps of forming an interconnecting pattern by trenches, burying the trenches with a conductor, and forming interconnecting lines will be described below. This interconnecting line formation method is used for high-packing-density semiconductor devices and generally called damascene process.

FIGS. 7A to 7E are sectional views showing the steps of forming interconnecting lines in order.

As shown in FIG. 7A, a CVD-oxide film (SiO_2) 3 and a plasma oxide film (SiO_2) 15 formed by plasma CVD are formed in this order on a silicon substrate 1. The CVD-oxide film 3 and the plasma oxide film 15 are insulating interlayers.

In FIG. 7B, the plasma oxide film 15 is so patterned as to form trenches 17 corresponding to an interconnecting pattern.

In FIG. 7C, copper (Cu) is deposited on the structure shown in FIG. 7B to form a copper film 16. This copper film 16 buries the trenches 17 and at the same time covers the surface of the plasma oxide film 15 on which the trenches 17 are formed.

In FIG. 7D, the polishing apparatus shown in FIG. 2 is used to perform CMP for the copper film 16 by using the plasma oxide film 15 as a stopper film, thereby planarizing the surface of the structure shown in FIG. 7C. This CMP step is done by using a polishing slurry, similar to the polishing slurry explained in the first embodiment, which is prepared by dispersing silicon nitride particles as polishing particles

in nitric acid as a solvent. As a consequence, dishing formed on the exposed surface of the copper film 16 is decreased. By this CMP, copper is buried only in the trenches 17 to complete buried interconnecting lines in the first layer.

Subsequently, as shown in FIG. 7E, silicon dioxide (SiO_2) is deposited on the structure shown in FIG. 7D by using plasma CVD, forming a plasma oxide film 18. Since the surface of the structure shown in FIG. 7D is accurately planarized, the plasma oxide film 18 is easily formed.

Also, forming buried interconnecting lines using the polishing slurry according to the present invention facilitates the formation of buried interconnecting lines in the second and third layers (not shown).

The secondary particle size dependence of the polishing rate will be described below.

FIG. 8 is a graph showing the relationship between the secondary particle size of polishing particles and the polishing rate. This secondary particle size dependence of the polishing rate was obtained by polishing polysilicon with a polishing slurry prepared by dispersing silicon nitride particles as polishing particles in nitric acid as a solvent.

Referring to FIG. 8, the ordinate indicates the polishing rate and the abscissa indicates the secondary particle size.

As shown in FIG. 8, when the secondary particle size is about 50 nm, the polishing rate is 41.2 nm/min. However, when the secondary particle size exceeds about 60 nm, the polishing rate greatly increases to 810.8 nm/min. When the secondary particle size is about 200 to 260 nm, the polishing rate is 1108.4 nm/min.

As described above, a polishing slurry containing silicon nitride polishing particles has a tendency to critically increase its polishing rate when the secondary particle size of the polishing particles exceeds about 60 nm.

When the particle size of polishing particles is small, polishing proceeds mainly due to the action of chemical polishing. As the particle size of polishing particles increases, the action of mechanical polishing becomes strong in polishing. It is estimated that the action of mechanical polishing is particularly significant in a polishing slurry containing silicon nitride polishing particles when the secondary particle size is about 60 nm.

The secondary particle size is preferably as large as possible. However, if the secondary particle size is too large, a number of flaws may be formed on the polished surface. If a conductor such as a metal enters these flaws, this may cause a short circuit. Therefore, the number of flaws is preferably as small as possible. For this reason, it is preferable that the secondary particle size do not exceed 300 nm. In addition, the particle size of secondary particles is preferably minimized as long as the polishing rate does not decrease. From these points of view, the particle size of secondary particles is particularly preferably about 60 to 100 nm.

As a solvent used in the polishing slurry of the present invention, it is possible to use an emulsifying agent, water, a surfactant, fats and oils, an adhesive, and ionized water, in addition to nitric acid. Also, an acidic solvent is primarily used as a solvent. One representative example is nitric acid. Examples of an alkaline solvent are ammonia, amines such as piperazine, and inorganic alkalis such as potassium hydroxide and sodium hydroxide. Any of these alkaline solvents can also be used as a solvent.

It is also possible to prepare a diluted polishing slurry by adding a dispersant, e.g., ionized water, to the polishing slurry according to the present invention. When a polishing

taneously and not necessary for polishing is collected through the ionized-water exhaust pipe 48 to the wasted-water pipe 45 to neutralize the wasted water created during polishing.

FIG. 11 is a sectional view of a CMP apparatus according to a sixth embodiment of the invention, showing an electrolytic bath. As is shown in FIG. 11, an electrolytic bath 42 has a cathode chamber 51 and an anode chamber 52. The cathode chamber 51 contains a cathode electrode 53, while the anode chamber 52 contains an anode electrode 54. These electrodes 53 and 54 are formed of platina or titanium. The cathode and anode chambers 51 and 52 are partitioned by a porous barrier membrane 55 for efficiently separating negative-ionized water 63 created in the cathode chamber 51, from positive-ionized water 64 created in the anode chamber 52. The cathode electrode 53 in the electrolytic bath 42 is connected to the negative electrode 57 of a battery 56, and the anode electrode 54 to the positive electrode 58 of the battery 56.

In the electrolytic bath 42, a diluent electrolyte solution 59, with a supporting electrolyte (e.g. ammonium chloride) contained therein is mixed with deionized water, and a power voltage is applied thereto from the battery 56, thereby electrolyzing the deionized water. Negative-ionized water 63 created on the side of the cathode electrode 53 as a result of electrolyzation is alkaline ionized water, while positive-ionized water 64 created on the side of the anode electrode 54 is acidic ionized water. Moreover, if deionized water is electrolyzed in the bath 42 using oxalic acid as the supporting electrolyte, both negative-ionized water created on the side of the cathode and positive-ionized water created on the side of the anode exhibit acidic properties. The negative-ionized water 63 in the cathode chamber 51 is supplied to the outside through a negative-ionized water supply pipe 61, and the positive-ionized water in the anode chamber 52 is supplied to the outside through a positive-ionized water supply pipe 62.

Since alkaline ionized water is usually created in the cathode chamber 51, the negative-ionized water supply pipe 61 connected to the electrolytic bath 42 is used, in the sixth embodiment, as the ionized-water supply pipe 40 for supplying alkaline ionized water to the polishing pad 25, when polishing is performed using alkaline ionized water. In this case, acidic ionized water created in the anode chamber 52 is not necessary and hence exhausted. Accordingly, the positive-ionized water supply pipe 62 is used as the ionized water exhaust pipe 48 for exhausting ionized water, and connected to the wasted water pipe 45. On the other hand, if polishing is performed using acidic ionized water, the positive-ionized water supply pipe 62 connected to the electrolytic bath 42 is used as the ionized-water supply pipe 40 for supplying acidic ionized water to the polishing pad 25. In this case, alkaline ionized water created in the cathode chamber 51 is not necessary and hence exhausted. Thus, the negative-ionized water supply pipe 61 is used as the ionized water exhaust pipe 48 for exhausting ionized water, and connected to the wasted water pipe 45. (See FIG. 10).

Ionized water can be classified into alkaline ionized water and acidic ionized water. Ionized water of a desired pH is created by electrolyzing, at a low voltage, deionized water which contains no electrolyte, i.e. no metal impurity, in an electrolytic bath with a solid electrolyte contained therein. Where in the case of using alkaline ionized water, the polishing rate is changed during polishing, it can be increased in a stable manner by increasing the pH value of alkaline ionized water, and can be reduced in a stable manner by reducing the pH value of alkaline ionized water.

On the other hand, in the case of using acidic ionized water, the polishing rate can be increased in a stable manner by reducing the pH value of acidic ionized water, and can be reduced in a stable manner by increasing the pH value of acidic ionized water.

Whether alkaline ionized water or acidic ionized water is used depends upon the kind of a film deposited on a semiconductor wafer.

Ionized water can electrically stabilize the surface of the film deposited on the wafer obtained after polishing. Acidic ionized water is suitable for a deposit film made of a metal with a high melting point, such as Al, Cu, W, etc. Such a deposit film has its surface oxidized by acidic ionized water after polishing, with the result that the potential of the surface is stabilized.

Alkaline ionized water or acidic water is suitable for a deposit film made of silicon oxide (SiO_2), silicon nitride (Si_3N_4), polysilicon or monocrystalline silicon. Alkaline ionized water can electrically stabilize the surface of such a deposit film. Alkaline ionized water should be used case where a SiO_2 film is polished, and case where a polysilicon film is polished. On the other hand, acidic ionized water should be used case where a Cu film is polished.

Conditions such as the polishing rate, the degree of stabilization of a deposit film, etc. depend upon the pH value of ionized water. Therefore, adjustment of the pH value of ionized water is very important to set optimal polishing conditions. Since the pH value of ionized water depends upon its temperature, it can be accurately adjusted by controlling the temperature of ionized water. The pH value of acidic ionized water increases as its temperature increases, whereas that of alkaline ionized water reduces as its temperature increases. Further, the rate of change in pH is higher in alkaline ionized water than in acidic ionized water.

Conventionally, polishing slurries are roughly classified into two categories: one is an oxide-based polishing slurry and the other is a metal-based polishing slurry. The oxide-based polishing slurry is represented by a polishing slurry containing silica polishing particles. The metal-based polishing slurry is represented by a polishing slurry containing alumina polishing particles. The oxide-based polishing slurry is used in polishing of silicon and silicon oxide. The metal-based polishing slurry is used in polishing of tungsten, copper, and aluminum. That is, polishing slurries are selected in accordance with the substances to be polished in the fabrication of semiconductor devices.

A polishing slurry containing silicon nitride polishing particles, however, can singly polish all of silicon, silicide silicon oxide, silicon nitride tungsten, copper, gold and aluminum.

In addition, a polishing slurry containing silicon nitride polishing particles can polish suicides such as glass and therefore can be used in polishing of, e.g., liquid-crystal screens and lenses. This remarkably widens the range of uses of this polishing slurry.

Furthermore, an equivalent effect can be obtained by using silicon carbide or graphite, particularly carbon graphite, instead of silicon nitride, as polishing particles.

Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details and representative embodiments shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalent.



US005783489A

United States Patent [19]

Kaufman et al.

[11] Patent Number: **5,783,489**[45] Date of Patent: **Jul. 21, 1998**[54] **MULTI-OXIDIZER SLURRY FOR
CHEMICAL MECHANICAL POLISHING**[75] Inventors: **Vlasta Brusic Kaufman**, Geneva;
Shumin Wang, Naperville, both of Ill.[73] Assignee: **Cabot Corporation**, Boston, Mass.[21] Appl. No.: **718,937**[22] Filed: **Sep. 24, 1996**[51] Int. Cl.⁶ **B44C 1/22**[52] U.S. Cl. **438/692; 438/693; 252/79.2;**
51/308; 51/309; 106/3[58] Field of Search **438/692, 693;**
252/79.2; 51/308, 309; 106/3[56] **References Cited****U.S. PATENT DOCUMENTS**

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Primary Examiner—Deborah Jones[57] **ABSTRACT**

A chemical mechanical polishing slurry comprising at least two oxidizing agents, an organic acid and an abrasive and a method for using the chemical mechanical polishing slurry to remove titanium, titanium nitride, and an aluminum alloy containing layer from a substrate.

38 Claims, No Drawings

MULTI-OXIDIZER SLURRY FOR CHEMICAL MECHANICAL POLISHING

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention concerns a chemical mechanical polishing slurry including at least two oxidizers. The chemical mechanical polishing slurry is useful for polishing metal layers and thin-films associated with semiconductor manufacturing. More particularly this invention concerns a chemical mechanical polishing slurry that is especially adapted for polishing multiple metal layers and thin-films where one of the layers or films is comprised of aluminum or an aluminum containing alloy and another layer or thin film is comprised of titanium or a titanium containing alloy such as titanium nitride.

2. Description of the Art

Integrated circuits are made up of millions of active devices formed in or on a silicon substrate. The active devices, which are initially isolated from one another, are interconnected to form functional circuits and components. The devices are interconnected through the use of well-known multilevel interconnections. Interconnection structures normally have a first layer of metallization, an interconnection layer, a second level of metallization, and sometimes a third and subsequent level of metallization. Interlevel dielectrics such as doped and undoped silicon dioxide (SiO_2), are used to electrically isolate the different levels of metallization in a silicon substrate or well. The electrical connections between different interconnection levels are made through the use of metallized vias. U.S. Pat. No. 4,789,648, which is incorporated herein by reference, describes a method for preparing multiple metallized layers and metallized vias in insulator films. In a similar manner, metal contacts are used to form electrical connections between interconnection levels and devices formed in a well. The metal vias and contacts may be filled with various metals and alloys including titanium (Ti), titanium nitride (TiN), tantalum (Ta), aluminum copper (Al—Cu), aluminum silicon (Al—Si), copper (Cu), tungsten (W), and combinations thereof. The metal vias and contacts generally employ an adhesion layer such as titanium nitride (TiN) and/or titanium (Ti) to adhere the metal layer to the SiO_2 substrate. At the contact level, the adhesion layer acts as a diffusion barrier to prevent the filled metal and SiO_2 from reacting.

In one semiconductor manufacturing process, metallized vias or contacts are formed by a blanket metal deposition followed by a chemical mechanical polish (CMP) step. In a typical process, via holes are etched through an interlevel dielectric (ILD) to interconnection lines or to a semiconductor substrate. Next, a thin adhesion layer such as titanium nitride and/or titanium is generally formed over the ILD and is directed into the etched via hole. Then, a metal film is blanket deposited over the adhesion layer and into the via hole. Deposition is continued until the via hole is filled with the blanket deposited metal. Finally, the excess metal is removed by chemical mechanical polishing, (CMP) to form metal vias. Processes for manufacturing and/or CMP of ILD's are disclosed in U.S. Pat. Nos. 4,671,851, 4,910,155 and 4,944,836.

In a typical chemical mechanical polishing process, the substrate is placed in direct contact with a rotating polishing pad. A carrier applies pressure against the backside of the substrate. During the polishing process, the pad and table are rotated while a downward force is maintained against the substrate back. An abrasive and chemically reactive

solution, commonly referred to as a "slurry" is applied to the pad during polishing. The slurry initiates the polishing process by chemically reacting with the film being polished. The polishing process is facilitated by the rotational movement of the pad relative to the substrate as slurry is provided to the wafer/pad interface. Polishing is continued in this manner until the desired film on the insulator is removed.

The slurry composition is an important factor in the CMP step. Depending on the choice of the oxidizing agent, the abrasive, and other useful additives, the polishing slurry can be tailored to provide effective polishing to metal layers at desired polishing rates while minimizing surface imperfections, defects and corrosion and erosion. Furthermore, the polishing slurry may be used to provide controlled polishing selectivities to other thin-film materials used in current integrated circuit technology such as titanium, titanium nitride and the like.

Typically CMP polishing slurries contain an abrasive material, such as silica or alumina, suspended in an oxidizing, aqueous medium. For example, U.S. Pat. No. 5,244,534 to Yu et al. reports a slurry containing alumina, hydrogen peroxide, and either potassium or ammonium hydroxide that is useful to remove tungsten at predictable rates with little removal of the underlying insulating layer. U.S. Pat. No. 5,209,816 to Yu et al. discloses a slurry comprising perchloric acid, hydrogen peroxide and a solid abrasive material in an aqueous medium that is useful for polishing aluminum. U.S. Pat. No. 5,340,370 to Cadien and Feller discloses a tungsten polishing slurry comprising approximately 0.1M potassium ferricyanide, approximately 5 weight percent silica and potassium acetate. Acetic acid is added to buffer the pH at approximately 3.5.

U.S. Pat. No. 4,789,648 to Beyer et al. discloses a slurry formulation using alumina abrasives in conjunction with sulfuric, nitric, and acetic acids and deionized water. U.S. Pat. Nos. 5,391,258 and 5,476,606 disclose slurries for polishing a composite of metal and silica which includes an aqueous medium, abrasive particles and an anion which controls the rate of silica removal. Other polishing slurries for use in CMP applications are described in U.S. Pat. No. 5,527,423 to Neville et al., U.S. Pat. No. 5,354,490 to Yu et al., U.S. Pat. No. 5,340,370 to Cadien et al., U.S. Pat. No. 5,209,816 to Yu et al., U.S. Pat. No. 5,157,876 to Medellin, U.S. Pat. No. 5,137,544 to Medellin, and U.S. Pat. No. 4,956,313 to Cote et al.

It has been recognized that CMP slurries that are used to polish multiple metal layers in a single step typically exhibit a low polishing rate towards at least one of the metal layers. As a result, the polishing step is lengthened or operated at aggressive polishing conditions that can cause undesirable erosion of the SiO_2 layer and recessing of the metal vias and/or metal lines. Such recessing causes a non-planar via layer or metal line layer to be formed which impairs the ability to print high resolution lines during subsequent photolithography steps and can cause the formation of voids or open circuits in the formed metal interconnections. Additionally, recessing increases when over polishing is used to ensure complete removal of the titanium, titanium nitride, and aluminum films across the surface of a wafer. Thus, a need remains for CMP slurries which reliably polish a plurality of metal layers including a titanium layer in an integrated circuit. Accordingly, a new CMP polishing slurry that polishes titanium at a higher rate is needed to overcome the present substrate manufacturing reliability issues.

SUMMARY OF THE INVENTION

The present invention is directed to a single chemical mechanical polishing slurry that is able to polish aluminum alloy, titanium, and titanium nitride layers at acceptable rates.

In addition, the chemical mechanical polishing slurry has a low insulator polishing selectivity while exhibiting high polishing selectivities towards titanium, titanium nitride, and aluminum.

Furthermore, this invention is directed to methods for using a single chemical mechanical polishing slurry to polish a plurality of metal layers in an integrated circuit.

In one embodiment, this invention is an aqueous chemical mechanical polishing slurry. The chemical mechanical polishing slurry comprises an abrasive, from about 0.2 to about 10.0 weight percent of a first oxidizer, from about 0.5 to about 10.0 weight percent of a second oxidizer, and from about 0.5 to about 3.0 weight percent of at least one organic acid. The chemical mechanical polishing slurry should have a pH of from about 2.0 to about 8.0.

In another embodiment, this invention is an aqueous chemical mechanical polishing slurry. The chemical mechanical polishing slurry comprises alumina, from about 0.2 to about 10.0 weight percent ammonium persulfate, from about 0.5 to about 10.0 weight percent hydrogen peroxide, and from about 0.5 to about 3.0 succinic acid. Furthermore, the pH of the chemical mechanical polishing slurry ranges from about 2.0 to about 8.0.

In still another embodiment, this invention is a method for polishing a substrate. The method includes admixing an abrasive, from about 0.2 to about 10.0 weight percent of a first oxidizer, from about 0.5 to about 10.0 weight percent of a second oxidizer, from about 0.5 to about 3.0 weight percent of at least one organic acid, and deionized water to give a chemical mechanical polishing slurry. Next, the chemical mechanical polishing slurry is applied to the substrate and at least a portion of a titanium layer, at least a portion of a titanium nitride adhesion layer and at least a portion of an aluminum alloy containing layer associated with the substrate are removed by bringing a pad into contact with the substrate and moving the pad in relation to the substrate.

DESCRIPTION OF THE CURRENT EMBODIMENT

The present invention relates to a chemical mechanical polishing slurry that comprises an abrasive and at least two oxidizers. The chemical mechanical polishing slurry is used to polish at least one metal layer associated with a substrate selected from the group including integrated circuits, thin films, multiple level semiconductors, and wafers. In particular, the chemical mechanical polishing slurry of this invention has been found to exhibit excellent polishing selectivities when used to polish a substrate including titanium, titanium nitride, and aluminum alloy containing layers in a single step, multiple metal layer chemical mechanical polishing process.

Before describing the details of the various preferred embodiments of this invention, some of the terms that are used herein will be defined. The chemical mechanical polishing slurry, ("CMP slurry"), is a useful product of this invention that comprises an at least two oxidizing agents, an abrasive, an organic acid, and other optional ingredients. The CMP slurry is useful for polishing a multiple level metallization which may include but are not limited to semiconductor thin-films, integrated circuit thin-films, and for any other films and surfaces where CMP processes are useful. The terms "aluminum" and "aluminum containing alloys" are used interchangeably herein as it is within the understanding of one of skill in the art that pure aluminum is a poor conductor and that most "aluminum" containing

metallization layers are actually comprised of an aluminum containing alloy, such as Al—Cu, that are good conductors.

The oxidizing agents useful in the chemical mechanical polishing slurry are incorporated into a CMP slurry to aid in oxidizing the multiple metal layers to their corresponding oxide, hydroxide, or ions. For example, in the present invention, the oxidizing agents may be used to oxidize a metal layer to its corresponding oxide or hydroxide, e.g., titanium to titanium oxide, tungsten to tungsten oxide, copper to copper oxide, and aluminum to aluminum oxide. The oxidizing agents of this invention are useful when incorporated into a polishing slurry to polish metals and metal based components including titanium, titanium nitride, tantalum, copper, tungsten, aluminum, and aluminum alloys such as aluminum/copper alloys, and various mixtures and combinations thereof by mechanically polishing the metals to remove the respective oxide layer.

The CMP slurry of this invention includes at least two oxidizers. The first oxidizer is selected from peroxy compounds which may disassociate through hydroxy radicals. Such oxidizers exhibit good polishing selectivity towards titanium. Non-exclusive examples of such peroxy compounds include peracetic acid, urea hydrogen peroxide, sodium peroxide, perboric acid, sodium percarbonate, and hydrogen peroxide, with hydrogen peroxide being the preferred first oxidizer. The first oxidizer may be present in the overall chemical mechanical polishing slurry in an amount ranging from about 0.5 to about 10.0 weight percent. It is preferred that the first oxidizer is present in the slurry in an amount ranging from about 1.0 to about 6.0 weight percent and most preferably from about 2.0 to about 4.0 weight percent.

The CMP slurry of this invention includes a second oxidizer. The second oxidizer should be capable of CMP polishing of aluminum and aluminum containing alloy metal layers with good selectivities. The second oxidizer is selected from dipersulfate and monopersulfate compounds. Ammonium persulfate is a preferred second oxidizer. The second oxidizer may be present in the chemical mechanical polishing slurry in an amount ranging from about 0.2 to about 10.0 weight percent. More preferably, the second oxidizer will be present in the chemical mechanical polishing slurry in an amount ranging from about 2.0 to about 8.0 weight percent with a range of from about 3.0 to about 5.0 being most preferred.

The CMP slurry of this invention includes an abrasive. The abrasive is typically a metal oxide abrasive. The metal oxide abrasive may be selected from the group including alumina, titania, zirconia, germania, silica, ceria and mixtures thereof. The CMP slurry of this invention preferably includes from about 1.0 to about 9.0 weight percent or more of an abrasive. It is more preferred, however, that the CMP slurry of this invention includes from about 3.0 to about 6.0 weight percent abrasive.

The metal oxide abrasive may be produced by any techniques known to those skilled in the art. Metal oxide abrasives can be produced using any high temperature process such as sol-gel, hydrothermal or plasma process, or by processes for manufacturing fumed or precipitated metal oxides. Preferably, the metal oxide is a fumed or precipitated abrasive and, more preferably it is a fumed abrasive such as fumed silica or fumed alumina. For example, the production of fumed metal oxides is a well-known process which involves the hydrolysis of suitable feedstock vapor (such as aluminum chloride for an alumina abrasive) in a flame of hydrogen and oxygen. Molten particles of roughly spherical

shapes are formed in the combustion process, the diameters of which are varied through process parameters. These molten spheres of alumina or similar oxide, typically referred to as primary particles, fuse with one another by undergoing collisions at their contact points to form branched, three dimensional chain-like aggregates. The force necessary to break aggregates is considerable and often considered irreversible. During cooling and collecting, the aggregates undergo further collision that may result in some mechanical entanglement to form agglomerates. Agglomerates are thought to be loosely held together by van der Waals forces and can be reversed, i.e., de-agglomerated, by proper dispersion in a suitable media.

Precipitated abrasives may be manufactured by conventional techniques such as by coagulation of the desired particles from an aqueous medium under the influence of high salt concentrations, acids or other coagulants. The particles are filtered, washed, dried and separated from residues of other reaction products by conventional techniques known to those skilled in the art.

A preferred metal oxide will have a surface area, as calculated from the method of S. Brunauer, P. H. Emmet, and I. Teller, *J. Am. Chemical Society*, Volume 60, Page 309 (1938) and commonly referred to as BET, ranging from about 5 m²/g to about 430 m²/g and preferably from about 30 m²/g to about 170 m²/g. Due to stringent purity requirements in the IC industry the preferred metal oxide should be of a high purity. High purity means that the total impurity content, from sources such as raw material impurities and trace processing contaminants, is typically less than 1% and preferably less than 0.01% (i.e., 100 ppm).

In this preferred embodiment, the metal oxide abrasive consists of metal oxide aggregates having a size distribution less than about 1.0 micron, a mean aggregate diameter less than about 0.4 micron and a force sufficient to repel and overcome the van der Waals forces between abrasive aggregates themselves. Such metal oxide abrasive has been found to be effective in minimizing or avoiding scratching, pit marks, divots and other surface imperfections during polishing. The aggregate size distribution in the present invention may be determined utilizing known techniques such as transmission electron microscopy (TEM). The mean aggregate diameter refers to the average equivalent spherical diameter when using TEM image analysis, i.e., based on the cross-sectional area of the aggregate. By force is meant that either the surface potential or the hydration force of the metal oxide particles must be sufficient to repel and overcome the van der Waals attractive forces between the particles.

In another preferred embodiment, the metal oxide abrasive may consist of discrete, individual metal oxide particles having a primary particle diameter less than 0.4 micron (400 nm) and a surface area ranging from about 10 m²/g to about 250 m²/g.

Preferably, the metal oxide abrasive is incorporated into the aqueous medium of the polishing slurry as a concentrated aqueous dispersion of metal oxides, which aqueous dispersion of metal oxide abrasives typically ranges from about 3% to about 45% solids, and preferably between 10% and 20% solids. The aqueous dispersion of metal oxides may be produced utilizing conventional techniques, such as slowly adding the metal oxide abrasive to an appropriate media, for example, deionized water, to form a colloidal dispersion. The dispersion is typically completed by subjecting it to high shear mixing conditions known to those skilled in the art. The pH of the slurry may be adjusted away from the isoelectric point to maximize colloidal stability.

The CMP slurry of this invention includes an organic acid. A wide range of conventional organic acids, salts of organic acids, and mixtures thereof are useful in the CMP slurry of the present invention to enhance the selectivity to oxide polishing rate, such as monofunctional acids, di-functional acids, hydroxyl/carboxylate acids, chelating, non-chelating acids, and their salts. Preferably, the organic acid is selected from the group of acetic acid, adipic acid, butyric acid, capric acid, caproic acid, caprylic acid, citric acid, glutaric acid, glycolic acid, formic acid, fumaric acid, lactic acid, lauric acid, malic acid, maleic acid, malonic acid, myristic acid, oxalic acid, palmitic acid, phthalic acid, propionic acid, pyruvic acid, stearic acid, succinic acid, tartaric acid, valeric acid and derivatives, including salts thereof.

The organic acid or salt should be present in the final CMP slurry, individually or in combination with other organic acids or salts, in an amount sufficient to enhance the oxide selectivity without detrimentally effecting the stability of the CMP slurry. As such, the organic acid is typically present in the slurry from about 0.05% to 15% by weight, and preferably in a range between 0.5% and 5.0% by weight. Examples of chemical mechanical polishing slurries including organic acids and salts thereof are disclosed in U.S. Pat. Application Ser. No. 08/644,509 which is incorporated herein by reference. A preferred organic acid is succinic acid. Succinic acid has been found to promote passivation of aluminum and it also inhibits the removal of the dielectric layer.

Other well known polishing slurry additives may be incorporated into the chemical mechanical polishing slurry of this invention. One type of optional additives are inorganic acids and/or salts thereof which may be added to the polishing slurry to further improve or enhance the polishing rate of the barrier layers in the wafer, such as titanium and tantalum. Useful inorganic additives include sulfuric acid, phosphoric acid, nitric acid, ammonium salts, potassium salts, sodium salts or other cationic salts of sulfates and phosphates.

In order to promote stabilization of the polishing slurry including oxidizing agents against settling, flocculation and decomposition, a variety of optional additives, such as surfactants, stabilizers, or dispersing agents, can be used. If a surfactant is added to the CMP slurry, then it can be an anionic, cationic, nonionic, or amphoteric surfactant or a combination of two or more surfactants can be employed. Furthermore, it has been found that the addition of a surfactant may be useful to improve the within-wafer-non-uniformity (WIWNU) of the wafers, thereby improving the surface of the wafer and reducing wafer defects. Non-limiting examples of preferred stabilizers useful in the CMP slurry of this invention include but are not limited to phosphonic acids such as aminotri(methylenephosphonic) acid, 1-hydroxyethylidene-4-diphosphonic acid, hexamethylenediaminetetramethylene phosphonic acid, and diethylenetetramine pentamethylenephosphonic acid. One or more stabilizers may be present in the CMP slurry of this invention in an amount that is sufficient to produce measurable improvements in slurry stability, and generally in an amount ranging from about 100 ppm to about 5.0 weight percent.

In general, the amount of additive such as a surfactant that may be used in the present invention should be sufficient to achieve effective stearic stabilization of the slurry and will typically vary depending on the particular surfactant selected and the nature of the surface of the metal oxide abrasive. For example, if not enough of a selected surfactant is used, it will have little or no effect on stabilization. On the other hand, too much surfactant in the CMP slurry may

result in undesirable foaming and/or flocculation in the slurry. As a result, stabilizers such as surfactants should generally be present in a range between about 0.001% and 10% by weight. Furthermore, the additive may be added directly to the slurry or treated onto the surface of the metal oxide abrasive utilizing known techniques. In either case, the amount of additive is adjusted to achieve the desired concentration in the polishing slurry.

Stabilizers most useful in the CMP slurry of this invention are phosphonic acids and salts thereof. A most preferred phosphonic acid stabilizer is aminotrimethylene phosphonic acid. A phosphonic acid stabilizer may be present in the CMP slurry of this invention in an amount ranging from about 0.01 to about 5.0 weight percent. The addition of one or more phosphonic acids to the CMP slurry of this invention may also inhibit metallic corrosion.

It is desirable to maintain the pH of the CMP slurry of this invention within a range of from about 2.0 to about 8, and preferably between from about 3.5 to about 6 in order to facilitate control of the CMP process. Specifically, it has been observed that the metal surface film passivation capability of the CMP slurry of this invention is compromised at high pH's, e.g., greater than 8. Likewise, slurry handling problems and substrate polishing quality problems are encountered when the pH of the CMP slurry of this invention is too low, e.g., less than 2. The pH of the CMP slurry of this invention may be adjusted using any known acid, base, or amine. However, the use of an acid or base that contains no metal ions, such as ammonium hydroxide and amines, or nitric, phosphoric, sulfuric, or organic acids are preferred to avoid introducing undesirable metal components into the CMP slurry of this invention.

The chemical mechanical polishing slurry of this invention has been found to have a high titanium (Ti) polishing rate as well as a high polishing rates towards titanium nitride (TiN) an aluminum containing layer and especially towards an Al—Cu metal layer. In addition, the chemical mechanical polishing slurry exhibits desirable low polishing rates towards the dielectric insulating layer.

One important application for the chemical mechanical polishing slurry of this invention is as a chemical mechanical polish for thin layer films comprising titanium, aluminum and aluminum containing alloys such as Al—Cu. In such a polishing application, the single polishing slurry is effective to polish titanium, titanium nitride, and aluminum alloy containing layers. The CMP slurry of this invention preferably exhibit a Al—Cu to titanium [Al—Cu:Ti] polishing selectivity and a Al—Cu to TiN [Al—Cu:TiN] polishing selectivity of from about 2:1 to about 1:2 and preferably from about 1:1.25 to about 1.25:1. At the same time the CMP slurry of this invention exhibits a very low dielectric (SiO₂) polishing rate and preferably an SiO₂ polishing rate less than 40Å/min.

The CMP slurry may be produced using conventional techniques known to those skilled in the art. Typically, the oxidizing agent and any optional additives, are mixed into the aqueous medium, such as deionized or distilled water, at pre-determined concentrations under low shear conditions until such components are completely dissolved in the medium. A concentrated dispersion of the metal oxide abrasive, such as fumed alumina, is added to the medium and diluted to the desired loading level of abrasive in the final CMP slurry.

The CMP slurries of the present invention may be supplied as one package system (oxidizing agents, abrasive, and additives in a stable aqueous medium). To avoid possible

CMP slurry degradation, however, it is preferred that at least a two package system is used where the first package comprises the first oxidizer and the second package comprises the second oxidizer. The remaining components, the abrasive, the organic acid, and any optional additives may be placed in either the first container, the second container or in a third container. Furthermore, the components in the first container or second container may be in dry form while the components in the corresponding container are in the form of an aqueous dispersion. For example, the first container may comprise the first oxidizer in aqueous form while the second container comprises an aqueous dispersion of the abrasive the second oxidizer and the organic acid. Alternately, the first container may comprise an aqueous dispersion of an abrasive and the first oxidizer while the second container may comprise the organic acid and the second oxidizer in aqueous form. Other two-container combinations of the ingredients of the CMP slurry of this invention are within the knowledge of one having ordinary skill in the art. It is preferred that the first oxidizer and the second oxidizer are held in separate containers as they may degrade over time when combined unless they are stored at low temperatures, e.g., 10° C. or less.

A multi-package CMP slurry system may be used with any standard polishing equipment appropriate for use on the desired metal layer of the wafer. The multi-package system includes one or more CMP slurry components in aqueous or dry form in two or more containers. The multi-package system is used by combining the components from the various containers in the desired amounts to give a CMP slurry comprising at least two oxidizing agents, an abrasive, and an organic acid in amounts described above.

The CMP slurry of the present invention does not significantly increase the silicon dioxide polishing rate above about 40Å/min. However, the CMP slurry of this invention significantly increases the polishing rate of titanium or titanium nitride while maintaining a high polishing rate towards aluminum and aluminum containing alloys such as Al—Cu. Thus, the CMP slurry of this invention is effective in controlling polishing selectivities of titanium, titanium nitride and Al—Cu. The polishing slurry of the present invention may be used during the various stages of semiconductor integrated circuit manufacture to provide effective polishing at desired polishing rates while minimizing surface imperfections and defects.

EXAMPLES

We have discovered that a CMP slurry including two oxidizers is capable of polishing a multiple metal layer comprising titanium, titanium nitride, and Al—Cu at high rates while exhibiting an acceptable low polishing rate towards the dielectric layer.

The following examples illustrate preferred embodiments of this invention as well as preferred methods for using compositions of this invention.

Example 1

In this example, CMP polishing was accomplished using two CMP slurries including 4.0 weight percent ammonium persulfate, 3.0 weight percent succinic acid, 5.0 weight percent of a fumed alumina abrasive, WA-355, manufactured by the Microelectronics Materials Division of Cabot Corporation, in Tuscola, Ill. and sold under the trademark SEMI-SPERSE®, and either 0 or 3.0 weight percent hydrogen peroxide with the remainder of the slurry consisting of deionized water. The slurry was adjusted to a pH of 5.0 with ammonium hydroxide.

The CMP slurry was applied to Ti coated blanket wafers. The wafers were placed in an IPEC 472 tool manufactured by IPEC Planar. The wafers were subjected to 5 psi down force, a table speed of 45 rpm, and a spindle speed of 60 rpm. The CMP slurry was applied to a XMGH 1158 pad manufactured by Rodel, Inc. at a rate of 200 ml/min.

The titanium removal rate for the CMP slurry containing no hydrogen peroxide was 8.6 nm/min and the titanium/Al—Cu selectivity was 40.7. The titanium removal rate for the CMP slurry containing 3.0 weight percent hydrogen peroxide was 200 nm/min and the titanium/Al—Cu selectivity was 1:1. In both tests the Al—Cu removal rate was about 200 nm/min.

Example 2

This example studies the effect of varying solution pH on the aluminum polishing rates and Ti, TiN, and SiO₂ selectivities of a CMP slurry of this invention. This example used a CMP slurry of this invention having the following composition; 4.0 weight percent ammonium persulfate; 3.0 weight percent succinic acid; 3.0 weight percent hydrogen peroxide; 5.0 weight percent alumina abrasive (WA-355) with the remainder being deionized water. The pH of the slurry was adjusted using ammonium hydroxide to give two slurries; the first with a pH of 3.5 and the second with a pH of 5.0.

The CMP slurry was applied to Al, Ti, TiN, and SiO₂ blanket coated wafers. The wafers were placed in a IPEC 472 tool and polished using a 5 psi down force, a table speed of 45 rpm, and a spindle speed of 60 rpm. The CMP slurry was applied to a XMGH1158 pad at a rate of 200 ml/min. Table 1, below summarizes the results of this example.

TABLE 1

	pH 3.5	pH 5.0
Al removal rate:	350 nm/min	600 nm/min
Al W/TWNU	7.6%	14%
Sel. to Ti	1.72:1	1.61:1
Sel. to TiN	1.79:1	3.9:1
Sel. to SiO ₂	88:1	n/m
Dishing, 50 μm*	57 nm	40.5 nm
Dishing, 128 μm**	198 nm	164 nm
Erosion	65 nm	54 nm

*the result is based on initial feature depth of 750 nm covered with 1.5 μm of AlCu.

**the result is based on initial feature depth of 750 nm covered with 0.8 μm of AlCu.

The polishing results, set forth in Table 1, above, clearly show that the CMP slurry of this invention is useful over a wide pH range.

Example 3

This example investigates the effect of the addition of phosphonic acids to a CMP slurry of this invention on titanium dissolution. A CMP slurry consisting of 4.0 weight percent ammonium persulfate, 3.0 weight percent succinic acid, 3.0 weight percent hydrogen peroxide, 5.0 weight percent alumina abrasive (WA-355), and deionized water was used in this example. The CMP slurry, with and without the addition of small amounts of aminotri (methylenephosphonic acid) was introduced into an electrochemical cell, and the Ti dissolution rate of the freshly abraded surface was evaluated by electrochemical techniques five minutes after abrasion had ceased. The results of the tests are set forth in Table 2 immediately below:

TABLE 2

Slurry pH	% Phosphonic Acid	Ti Dissolution Rate (Å/min)
3.5	0	3.4
5.0	0	6.0
5.0	0.1	3.0
5.0	0.5	1.3
5.0	1.0	1.0
8.05	0	68
8.05	1.0	3.4

The results of these examples demonstrate that a CMP slurring including a first oxidizer and a second oxidizer is useful, over a wide range of pH's in polishing multiple layers of metallization in a single polishing step. The results also demonstrate that the addition of a stabilizer to a CMP slurry of this invention inhibits corrosion of a metal layer of a metal substrate.

While the present invention has been described by means of specific embodiments, it will be understood that modifications may be made without departing from the spirit of the invention. The scope of the invention is not to be considered as limited by the description of the invention set forth in the specification and examples, but rather as defined by the following claims.

What we claim is:

1. A chemical mechanical polishing slurry comprising:
an aqueous medium of;
an abrasive;
from about 0.2 to about 10.0 weight percent of a first oxidizer;
from about 0.5 to about 10.0 weight percent of a second oxidizer; and
from about 0.5 to about 15.0 weight percent of at least one organic acid, wherein the pH of the chemical mechanical polishing slurry ranges from about 2.0 to about 8.0.

2. The chemical mechanical polishing slurry of claim 1 wherein the first oxidizer is at least one peroxy compound which may disassociate through hydroxyl radicals.

3. The chemical mechanical polishing slurry of claim 2 wherein the first oxidizer is hydrogen peroxide.

4. The chemical mechanical polishing slurry of claim 1 wherein the second oxidizer is at least one dipersulfate salt or acid or monopersulfate salt or acid.

5. The chemical mechanical polishing slurry of claim 4 wherein the second oxidizer is ammonium persulfate.

6. The chemical mechanical polishing slurry of claim 1 wherein the abrasive is a metal oxide.

7. The chemical mechanical polishing slurry of claim 5 wherein the metal oxide abrasive is selected from the group including alumina, ceria, germania, silica, titania, zirconia, and mixtures thereof.

8. The chemical mechanical polishing slurry of claim 1 wherein the abrasive is an aqueous dispersion of a metal oxide.

9. The chemical mechanical polishing slurry of claim 7 wherein the metal oxide abrasive consists of metal oxide aggregates having a size distribution less than about 1.0 micron and a mean aggregate diameter less than about 0.4 micron.

10. The chemical mechanical polishing slurry of claim 7 wherein the metal oxide abrasive consists of discrete, individual metal oxide spheres having a primary particle diameter less than 0.400 micron and a surface area ranging from about 10 m²/g to about 250 m²/g.

11. The chemical mechanical polishing slurry of claim 1 wherein the abrasive has a surface area ranging from about 5 m²/g to about 430 m²/g.

12. The chemical mechanical polishing slurry of claim 11 wherein the abrasive has a surface area of from about 30 m²/g to about 170 m²/g.

13. The chemical mechanical polishing slurry of claim 7 wherein the abrasive is selected from the group consisting of precipitated abrasives or fumed abrasives.

14. The chemical mechanical polishing slurry of claim 13 wherein the abrasive is selected from the group consisting of silica, alumina, and mixtures thereof.

15. The chemical mechanical polishing slurry of claim 1 wherein the organic acid is succinic acid.

16. The chemical mechanical polishing slurry of claim 1 further including a surfactant.

17. The chemical mechanical polishing slurry of claim 1 further including a stabilizer.

18. A chemical mechanical polishing slurry comprising:

an aqueous medium;

from about 1.0 to about 9.0 weight percent alumina;

from about 0.5 to about 10.0 weight percent hydrogen peroxide;

from about 0.2 to about 10.0 weight percent ammonium persulfate; and

from about 0.5 to about 5.0 weight percent succinic acid, wherein the pH of the chemical mechanical polishing slurry ranges from about 2.0 to about 8.0.

19. The chemical mechanical polishing slurry of claim 18 wherein hydrogen peroxide is present in the composition in an amount ranging from about 1.0 to about 6.0 weight percent.

20. The chemical mechanical polishing slurry of claim 18 wherein ammonium persulfate is present in the composition in an amount ranging from about 2.0 to about 8.0 weight percent.

21. The chemical mechanical polishing slurry of claim 18 wherein the alumina is present in the composition in an amount ranging from about 3.0 to about 6.0 weight percent.

22. The chemical mechanical polishing slurry of claim 18 including from about 100 ppm to about 5.0 weight percent of a stabilizer.

23. The chemical mechanical polishing slurry of claim 18 having a Ti/Al—Cu selectivity of from about 1:2 to about 2:1.

24. A method for polishing a substrate including at least one metal layer comprising the steps of:

(a) admixing, from about 1.0 to about 9.0 weight percent of an abrasive, from about 0.2 to about 10.0 weight percent of a first oxidizer, from about 0.5 to about 10.0 weight percent of a second oxidizer, from about 0.5 to about 3.0 weight percent of at least one organic acid, and deionized water to give a chemical mechanical polishing slurry;

(b) applying the chemical mechanical polishing slurry to the substrate; and

(c) removing at least a portion of the metal layer from the substrate by bringing a pad into contact with the substrate and moving the pad in relation to the substrate.

25. The method of claim 24 wherein the substrate includes a titanium adhesion layer and an aluminum alloy containing layer and wherein at least a portion of the titanium layer and at least a portion of the aluminum alloy containing layer are removed in step (c).

26. The method of claim 24 wherein the substrate further includes a titanium nitride layer wherein at least a portion of the titanium nitride layer is removed in step (c).

27. The method of claim 24 wherein the chemical mechanical polishing slurry is applied to the pad before the pad is placed into contact with the substrate.

28. The method of claim 24 wherein the first oxidizer is at least one peroxy compound that may disassociate through hydroxyl radicals.

29. The method of claim 28 wherein the first oxidizer is hydrogen peroxide.

30. The method of claim 24 wherein the second oxidizer is at least one dipersulfate salt or acid or monopersulfate salt or acid.

31. The method of claim 30 wherein the second oxidizer is ammonium persulfate.

32. The method of claim 24 wherein the abrasive is a metal oxide.

33. The method of claim 32 wherein the metal oxide abrasive is selected from the group including alumina, ceria, germania, silica, titania, zirconia, and mixtures thereof.

34. The method of claim 24 wherein the abrasive is an aqueous dispersion of a metal oxide.

35. The method of claim 34 wherein the metal oxide abrasive is selected from the group consisting of precipitated alumina, fumed alumina, precipitated silica, fumed silica, and mixtures thereof.

36. The method of claim 24 wherein the organic acid is succinic acid.

37. A method for polishing a substrate including a titanium adhesion layer, a titanium nitride layer and an aluminum alloy containing layer comprising:

(a) admixing, hydrogen peroxide, ammonium persulfate, succinic acid, and alumina with deionized water to give a chemical mechanical polishing slurry comprising from about 1.0 to about 9.0 weight percent alumina, from about 0.2 to about 10.0 weight percent ammonium persulfate, from about 0.5 to about 10.0 weight percent hydrogen peroxide, and from about 0.5 to about 3.0 succinic acid, wherein the pH of the chemical mechanical polishing slurry ranges from about 2.0 to about 8.0 and wherein the titanium to aluminum alloy polishing selectivity ranges from about 2:1 to about 1:2;

(b) applying the chemical mechanical polishing slurry to the substrate; and

(c) removing at least a portion of the titanium adhesion layer, at least a portion of the titanium nitride layer and at least a portion of the aluminum alloy layer by bringing a pad into contact with the substrate and moving the pad in relation to the substrate.

38. The method of claim 24 wherein the substrate is selected from the group consisting of integrated circuits, thin films, multiple level semiconductors, and wafers.

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,783,489
DATED : July 21, 1998
INVENTOR(S) : Kaufman et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

At column 12, line 48 insert -- Ti/Al-Cu -- before "ranges" and after "selectivity"

Signed and Sealed this
Fifteenth Day of February, 2000

Attest:



Q. TODD DICKINSON

Attesting Officer

Commissioner of Patents and Trademarks



US005759917A

United States Patent [19]

Grover et al.

[11] Patent Number: 5,759,917

[45] Date of Patent: Jun. 2, 1998

[54] COMPOSITION FOR OXIDE CMP

[75] Inventors: Gautam S. Grover, Lisle; Brian L. Mueller, Aurora, both of Ill.

[73] Assignee: Cabot Corporation, Boston, Mass.

[21] Appl. No.: 774,488

[22] Filed: Dec. 30, 1996

[51] Int. Cl.⁶ C03C 25/06; C23F 1/00

[52] U.S. Cl. 438/690; 106/11; 51/309;
156/653.1; 156/654.1; 438/692; 438/693

[58] Field of Search 106/3, 11; 51/306,
51/309; 156/653.1, 654.1; 252/79.1; 438/690,
692, 693

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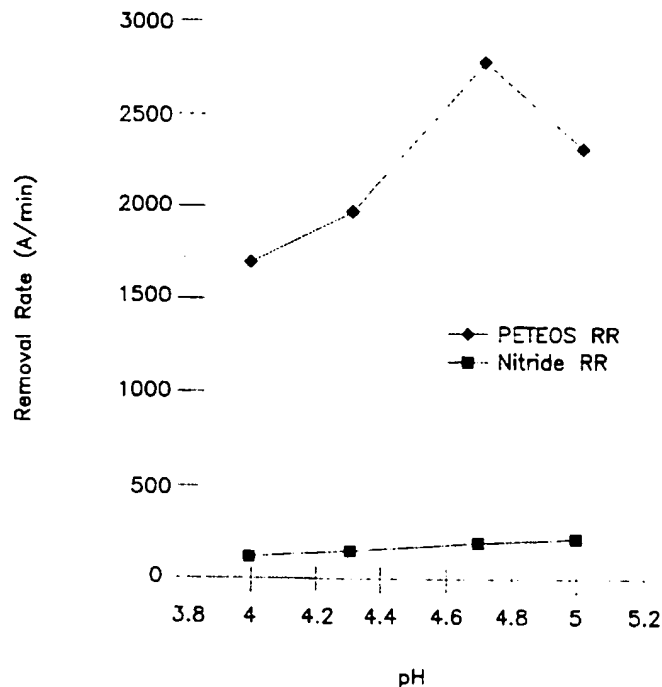
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Primary Examiner—Deborah Jones

[57] ABSTRACT

A chemical mechanical polishing composition comprising carboxylic acid, a salt and a soluble cerium compound at a pH above 3 and a method to selectively polish a silicon oxide overfill in preference to a silicon nitride film layer in a single step during the manufacture of integrated circuits and semiconductors.

35 Claims, 1 Drawing Sheet



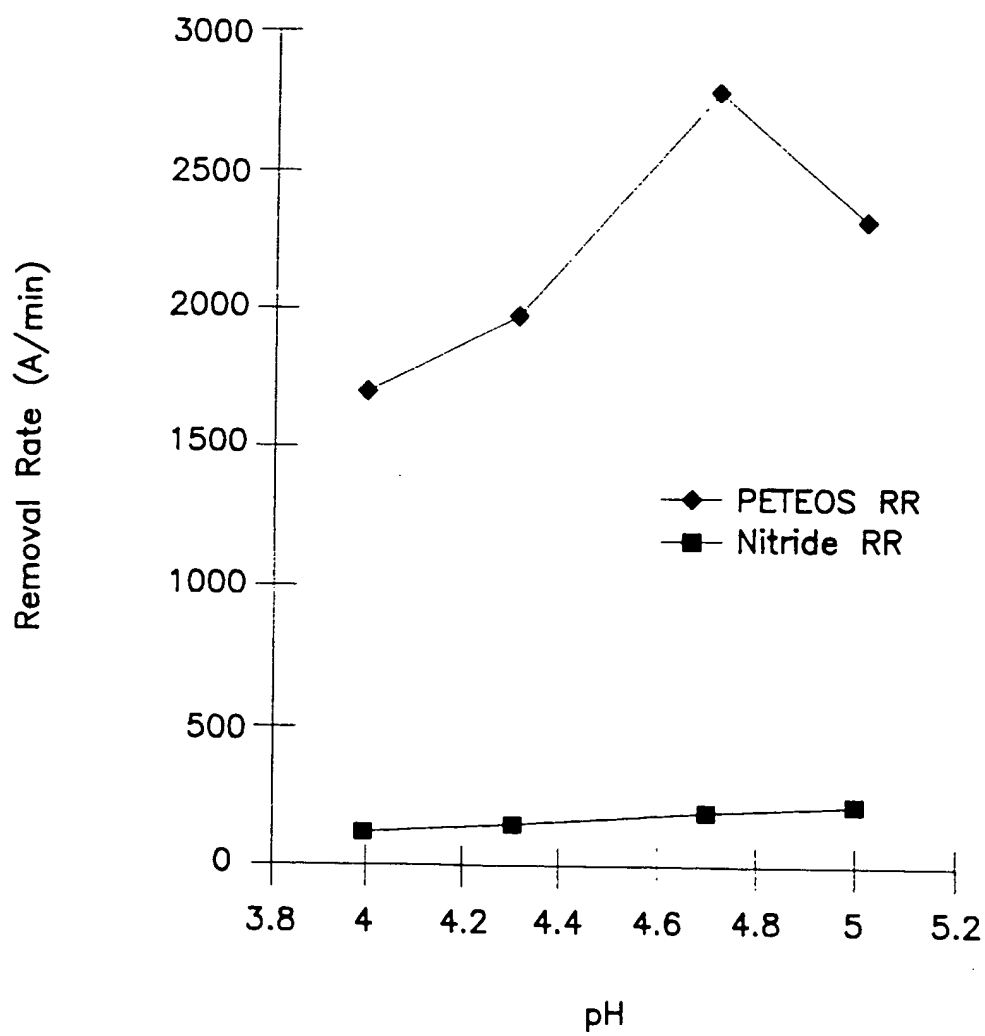


FIG. 1

COMPOSITION FOR OXIDE CMP

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to chemical mechanical polishing slurries for semiconductor integrated circuit substrates. Specifically, this invention is a CMP slurry having a unique chemistry that is especially suitable for chemical mechanical planarization where a high silicon dioxide removal rate, and a low silicon nitride removal rate are required on the same substrate.

2. Description of the Related Art

Integrated circuits (IC) are made up of millions of active devices formed in or on a silicon substrate. The active devices form functional circuits and components. These devices are then connected by the use of multilevel metallized interconnects and vias. Interconnection structures normally have a first layer metallization, an interconnect plug, a second layer of metallization, and sometimes a third or more layers of metallization with their respective interconnects. Inter level dielectrics (ILDs), such as doped and undoped SiO₂ are used to electrically isolate the different levels of interconnections.

Shallow trench isolation (STI) is a technology for device isolation in a give layer in the IC manufacturing process. In the STI process, silicon nitride is deposited on thermally grown oxide. After deposition of the nitride, a shallow trench is etched into the substrate using a mask. A layer of oxide is then deposited into the trench so that the trench forms an area of insulated dielectric which acts to isolate the devices in a chip, and thus reduces the cross-talk between active devices. The excess deposited oxide must be polished off and the trench planarized to prepare for the next level of metallization. The silicon nitride is applied to the silicon to prevent polishing of the masked silicon oxide of the device.

In a typical mechanical polishing process, the substrate is placed in direct contact with a rotating polishing pad. A carrier applies pressure against the backside of the substrate. During the polishing process, the pad and table are rotated while a downward force is maintained against the substrate back. An abrasive and chemically reactive solution, commonly referred to as "a CMP slurry", is flowed onto the pad during polishing. The chemicals and abrasive particles in the slurry initiate the polishing process by interacting with the wafer being polished. The polishing process is facilitated by the rotational movement of the pad relative to the substrate as slurry is provided to the wafer/pad interface. Polishing is continued in this manner until the final desired film thickness is achieved by removal of the required amount of thin-film material.

When polishing oxides, it is desirable of the slurry used to have a high removal rate towards the oxide layer and a low removal rate towards other layers which may be exposed during CMP, such as silicon nitride. The polishing slurry should be tailored to provide effective polishing at the desired polishing ranges selective to specific thin layer materials, while minimizing, at the same time, surface imperfections, defect, corrosion, erosion and the removal of silicon nitride and other stop layers.

CMP slurries useful for polishing oxides typically contain an abrasive at an alkaline or high pH. These slurries either rely on potassium hydroxide or ammonium hydroxide to effectively buffer the high pH. While these slurries polish silica at high rates they also polish silicon nitride at high rates. Typically, the ratio of these removal rates, i.e., the

selectivity is, at most, about 5 to 1 silicon oxide to silicon nitride. It is believed that the mechanism of silicon nitride polishing is oxidative hydrolysis of the nitride to the oxide in an aqueous environment. At alkaline pH this oxide and nitride are similarly etched at a high rate. Thus, present CMP slurries undesirably polish silicon nitride at an unacceptably high rate.

There remains a need in the semiconductor industry for CMP slurries that have greater than a 5 to 1 oxide to nitride selectivity. Accordingly, new CMP slurries that selectively remove the oxide at high rates while leaving the stop layer of silicon nitride relatively intact are needed to overcome the present manufacturing problems, increase throughput and reduce costs of the CMP process. This is because a low selectivity process, when used in a manufacturing environment, will necessarily suffer overpolishing—in thinner film parts of the wafer—and the nitride stop layer will not prevent breakthrough to the underlying thin film(s).

SUMMARY OF THE INVENTION

This invention is a chemical mechanical polishing composition that is capable of polishing a silicon dioxide layer at a high rate.

This invention is also a chemical mechanical polishing composition that inhibits the polishing of a silicon nitride film.

In addition, this invention is a method of using a chemical mechanical polishing composition that selectively removes silicon dioxide from a substrate while leaving a silicon nitride layer associated with the substrate essentially intact.

In one embodiment, this invention is a chemical mechanical polishing composition comprising carboxylic acid, a salt and a soluble cerium compound. The composition has a pH from about 3.0 to about 11, and preferably from about 3.8 to about 5.5 and is useful for selectively removing silicon dioxide from layered substrates.

In another embodiment, this invention is a chemical mechanical polishing slurry comprising the chemical mechanical polishing composition described above and an abrasive. The slurry is especially useful for silicon dioxide film polishing.

In still another embodiment, the present invention is a method for using a chemical mechanical polishing composition comprising a carboxylic acid, a salt and a soluble cerium compound in an aqueous solution having a pH from about 3.0 to about 11 to selectively remove oxide overfill in preference to a silicon nitride film layer during the manufacture of integrated circuits and semiconductors.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1—Plot of pH versus PETEOS removal rate and nitrate removal rate.

DESCRIPTION OF THE CURRENT EMBODIMENTS

The present invention is directed to a chemical mechanical polishing composition that comprises, a carboxylic acid, a salt, and a soluble cerium compound, having a pH of from about 3.0 to about 11.0. The chemical mechanical composition may be used alone or it may be combined with a metal oxide abrasive to form a slurry. The compositions and slurries of this invention polish oxide layers such as silicon dioxide layers associated with substrates at high rates. In addition, the compositions of this invention have been found to inhibit silicon nitride polishing. The present invention is

than about 10 weight percent of particles having a median particle size greater than 0.6 μm .

Precipitated cerium oxide is a suitable abrasive for oxide CMP. Precipitated cerium oxide particles are made from a variety of precursors including acetates, carbonates and hydroxide and nitrate salts of cerium. The median particle size of precipitated cerium oxide particles may range of from about 10 nm to about 500 nm, with the preferred size of precipitated cerium oxide particles being in the range of from about 30 to about 300 nm.

Another preferred abrasive is fumed silica. The production of fumed metal oxides is a well-known process which involves the hydrolysis of suitable feed stock vapor (such as silicon tetrachloride for a silica abrasive) in a flame of hydrogen and oxygen. Molten particles of roughly spherical shape are formed in the combustion process. The diameters of the particles are varied through process parameters, and these molten spheres of silica or similar oxide, typically referred to as primary particles, fuse with one another by colliding at their contact points to form branched, three dimensional chain-like aggregates. The force necessary to break aggregates is considerable and often irreversible. During cooling and collecting, the aggregates undergo further collisions that may result in some mechanical entanglement causing the formation of aggregates.

A preferred metal oxide will have a surface area, as calculated from the method of S. Brunauer, P. H. Emmet, and I. Teller, J. Am. Chemical Society, Volume 60, Page 309 (1938) and commonly referred to a BET, ranging from about 5 m^2/g to about 430 m^2/g and preferably from about 30 m^2/g to about 170 m^2/g . Due to stringent purity requirements in the IC industry the preferred metal oxide should be of a high purity. High purity means that the total impurity content, from sources such as raw material impurities and trace processing contaminants, is typically less than 1% and preferably less than 0.01% (i.e., 100 ppm).

In a preferred embodiment, the metal oxide abrasive consists of metal oxide aggregates having about 99 weight percent of the particles less than about 1.0 micron in diameter, a mean aggregate diameter less than about 0.4 micron and a force sufficient to repel and overcome the van der Waals forces between abrasive aggregates themselves. Such metal oxide abrasives have been effective in minimizing or avoiding scratching, pit marks, divots and other surface imperfections during polishing. The aggregate size distribution in the present invention may be determined using known techniques such as transmission electron microscopy (TEM). The mean aggregate diameter refers to the average equivalent spherical diameter when using TEM image analysis, i.e., based on the cross-sectional area of the aggregate. The surface potential or the hydration force of the metal oxide particles must be sufficient to repel and overcome the van der Waals attractive forces between the particles.

In another preferred embodiment, the metal oxide abrasive may consist of discrete metal oxide particles having a particle diameter less than 0.5 micron (500 nm) and a surface area ranging from about 10 m^2/g to about 250 m^2/g .

A CMP slurry of this invention will include from about 2 weight percent to about 25 weight percent metal oxide abrasive and preferably from about 2 weight percent to about 15 weight percent metal oxide abrasive.

Metal oxide abrasives useful in CMP slurries of the present invention are incorporated into the aqueous medium of the polishing slurry as a concentrated aqueous dispersion of metal oxides comprising from about 3% to about

55% solids, and preferably between 30% and 50% solids. The aqueous dispersion of metal oxides may be produced using conventional techniques, such as slowly adding the metal oxide abrasive to an appropriate media, for example, de-ionized water, to form a colloidal dispersion. The dispersions are typically completed by subjecting them to high shear mixing conditions known to those skilled in the art.

The abrasives useful in a CMP slurry of the present invention can be a mixture of the abrasives described above. For example, precipitated cerium oxide, pulverized cerium oxide (also referred to as ceria) and fumed silica could be incorporated into a CMP slurry of the present invention. Other combinations of abrasives are also useful in the CMP slurry. In addition, the mixture of abrasives could include any relative proportion of one abrasive to another. For example, a combination of from about 5 to 100 weight percent of the pulverized oxide abrasive described above with from about 0 to about 95 weight percent precipitated abrasive has been found to be effective as a CMP slurry abrasive in STI applications.

Commercially available precipitated cerium oxides sold at a pH of about 1.5, are ineffective as CMP slurries. We have, however, discovered that significantly increasing the pH of the commercially available slurry to about 3.5 results in a CMP slurry that is useful for STI polishing. Furthermore, we have surprisingly discovered that a CMP slurry with the composition and pH disclosed above exhibits a high oxide layer removal rate and low nitride layer removal rate.

The CMP slurry of this invention must have a pH from about 3.0 to about 11.0 to be effective. More preferably, the slurry pH will range from about 3.5 to about 6.0, and most preferably the pH is from about 3.8 to about 5.5. Slurry pH is adjusted by adding any base to the composition and preferably by adding a non-metal base such as ammonium hydroxide to the slurry.

In order to further stabilize a polishing slurry of this invention against settling, flocculation and decomposition of the oxidizing agent, a variety of additional optional additives, such as surfactants, polymeric stabilizers or other surface active dispersing agents, can be used. The surfactant can be anionic, cationic, nonionic, amphoteric and combinations of two or more surfactants can be employed. Furthermore, it has been found that the addition of a surfactant may be useful to improve the within-wafer-non-uniformity (WTWNU) of the wafers, thereby improving the surface of the wafer and reducing wafer defects.

In general, the amount of an additive used, such as a surfactant, in the present invention should be sufficient to achieve effective steric stabilization of the slurry and will typically vary depending on the particular surfactant selected and the nature of the surface of the metal oxide abrasive. For example, if not enough of a selected surfactant is used, it will have little or no effect on stabilization. On the other hand, too much of the surfactant may result in undesirable foaming and/or flocculation in the slurry. As a result, additives like surfactants should generally be present in a range between about 0.001% and 10% by weight. Furthermore, the additive may be added directly to the slurry or treated onto the surface of the metal oxide abrasive utilizing known techniques. In either case, the amount of additive is adjusted to achieve the desired concentration in the polishing slurry.

The chemical mechanical polishing compositions and slurries of this invention are capable of selectively removing the silicon dioxide layer from layered substrates at very high

TABLE 3

Slurry No.	pH	% total solids	% pulverized ceria in slurry	PETEOS RR (Å/min)	Nitride RR (Å/min)	Selectivity
11	4	8	20	1595	108.4	14.71
12	4	8	40	2168	183.4	11.82
13	4	8	60	3356	826.5	4.06
14	4	8	80	4785	209.1	22.88

The results indicate that a CMP slurry including 80% pulverized ceria and 20% precipitated ceria produced the most desired properties of high PETEOS rates, low nitride rates and high selectivity.

EXAMPLE 6

Chemical Formulation Using Pulverized Ceria

A slurry, composed of L-90, a fumed silica particles manufactured by Cabot Corporation and sold under the trademark CAB-O-SIL®, ammonium cerium nitrate, acetic acid, of varying percentages, and deionized water was formulated as shown in Table 4. All slurries were adjusted to pH=4 after the inclusion of additives. The slurries were applied to substrate according to the methods described in Example 1.

TABLE 4

Slurry	weight % silica	weight % Amm. Cerium Nitrate	weight % Acetic Acid	Nitride RR (Å/min)	PETEOS RR (Å/min)	Selectivity
20	4	0.1	0.1	58	280	4.83
21	4	0.1	1	52	253	4.87
22	4	0.65	0.5	59	619	10.49
23	4	1	0.1	44	1535	34.89
24	4	1	1	312	1524	4.88
25	4	1	0	104.62	1337.9	12.79
26	4	2	0.05	57.51	1103	19.18
27	4	3	0.1	89.99	835.8	9.29
28	4	1	0.5	71.5	803.1	11.23
29	4	2	0.1	24.1	346.6	14.38
30	4	2	0.5	71.1	768.0	10.8

High PETEOS removal rates and low nitride removal rates were obtained with high nitrate (1% nitrate) content and low (0.1%) acetic acid content.

EXAMPLE 7

Chemical Formulation Using Silica—pH Test

A slurry, composed of 4 weight percent CAB-O-SIL® L-90 fumed silica, 1.8 weight percent ammonium cerium nitrate, and 0.6 weight percent acetic acid of varying percentages was formulated as shown in Table 5. The pH of the slurries varied from between 4.0 to 5.0. The slurries were applied to substrate according to the methods described in Example 1.

TABLE 5

Slurry	weight % silica	pH	weight % Acetic Acid	Nitride RR	PETEOS RR	Selectivity
31	4	4.0	0.6	114	1713.7	15.03
32	4	4.3	0.6	141	1988.9	14.11

TABLE 5-continued

Slurry	weight % silica	pH	weight % Acetic Acid	Nitride RR	PETEOS RR	Selectivity
33	4	4.7	0.6	199	2810.5	14.12
34	4	5.0	0.6	219	2355	10.75

High PETEOS removal rates are obtained and selectivity was very good for each slurry. The results indicate that slurry pH has a strong effect on PETEOS removal rate and the optimum removal rate of oxide is achieved at about pH 4.7 (FIG. 1).

While the present invention has been described by means of specific embodiments, it will be understood that modifications may be made without departing from the spirit of the invention. The scope of the invention is not considered to be limited by the description of the invention set forth in the specification and examples, but rather defined by the following claims.

EXAMPLE 8

A composition composed of 1.8 wt % ammonium cerium nitrate, 0.8 wt % acetic acid, and deionized water was used to polish PETEOS and silicon nitride wafers according to the method of Example 1. The pH of the slurry was adjusted to 4.5. The composition polished PETEOS at 690 Å/min and silicon nitride at 23 Å/min, giving a PETEOS selectivity of 30.

What we claim is:

1. An aqueous chemical mechanical polishing composition comprising:

a salt;

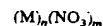
soluble cerium; and

a carboxylic acid, wherein the composition has a pH of from about 3 to about 11.

2. The aqueous chemical mechanical polishing composition of claim 1, wherein the pH is from about 3.8 to about 5.5.

3. The aqueous chemical mechanical polishing composition of claim 1, wherein the salt is a nitrate salt.

4. The aqueous chemical mechanical polishing composition of claim 3, wherein the nitrate salt is a compound having the formula:



wherein n and m are both integers and wherein when n=m, M is an alkali earth metal, H, NH₄ or NR₄ where R is an alkyl group having from 1 to 10 carbon atoms and wherein when n≠m, M is a multivalent cation or metal or a combination of multivalent cations and monovalent cations.

5. The aqueous chemical mechanical polishing composition of claim 3, including from about 0.05 to about 6.0 weight percent nitrate salt.

6. The aqueous chemical mechanical polishing composition of claim 3, wherein the nitrate salt is ammonium cerium nitrate.

7. The aqueous chemical mechanical polishing composition of claim 1, wherein the carboxylic acid is selected from the group consisting of monofunctional acids, di-functional acids and salts thereof.

8. The aqueous chemical mechanical polishing composition of claim 1, wherein the carboxylic acid is at least one compound selected from the group consisting of acetic acid, adipic acid, butyric acid, capric acid, caproic acid, caprylic

Appendix C

References In Support of Applicants' Position

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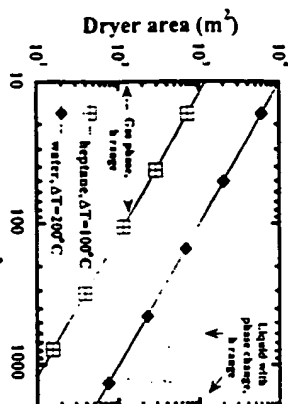


Figure 9 Dryer size for a 10^3 kg/year silica aerogel plant with density of 100 kg/m^3 .

where h is taken as the rate-controlling heat transfer coefficient. ΔT is governed by the solvent in the solid, the drying rate, and the maximum drying temperature which is fixed by the energy source (steam, direct fire, etc.). However, the heat transfer coefficient, assuming gas phase rate control, has a limited range. For drying from either heptane or water, the dryer size for a typical aerogel plant is shown in Figure 9. The drying of aerogels can be achieved in much smaller dryers when extractive drying is employed since the heat transfer coefficients are much larger than for gas phase heat transfer.¹¹

CONCLUSIONS

Drying of nano-size materials, either gels or particle slurries, can have a dramatic effect on both properties as well as process economics. By selecting the proper drying solvent and drying conditions, capillary pressure-induced shrinkage can be minimized. In certain cases, the use of surface passivation can be employed to further reduce drying damage. The role of drying solvent and drying conditions also has a significant impact on the overall process economics.

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If hexadecane is employed instead of water, the heat of vaporization per volume is an order of magnitude lower which results in an energy consumption decrease of the same magnitude and a capital decrease of over four times (via the 6/10's rule).

The heat of vaporization and the solids content fix the amount of energy which is required in the dryer per pound of product produced (note: the total energy required will be much higher since solvent condensation and recycle is required). With the total energy input fixed, the dryer size (surface area) is governed by the temperature driving force in the dryer (related to the difference in the wet bulb temperature and the dryer wall) and the heat transfer coefficient. This is described as $Q = hA\Delta T$

FABRICATION OF AGGLOMERATE-FREE NANOPOWDERS BY

HYDROTHERMAL CHEMICAL PROCESSING

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ABSTRACT

A chemical processing technique for the fabrication of nanopowders has been developed. The route is based on precipitation processes in solutions, either within aqueous droplets in micro-emulsions in the presence of surface modifiers like surfactants or by direct precipitation in solutions in the presence of these surface modifiers or small organic molecules directly bonded to the particle surface. In order to obtain well crystallized or densified particles, a continuous flow hydrothermal process has been developed which allows the fabrication of agglomerate-free surface modified nanopowders. The surface modification provides a full redispersibility after drying and permits a water-based processing. Nanoparticles preparation for ZnO , ITO and ATO by this route are described.

INTRODUCTION

The interest in nanopowders has constantly increased over the past years for scientific as well as for industrial reasons. This is based on the early work of Gleiter, who stated that nanostructured ceramic materials may have extraordinary properties, such as plastic deformation abilities [1, 2]. Meanwhile, various methods have been developed for the preparation of ceramic nano-scale powders, mainly based on gas phase reactions such as vapor phase condensation, chemical vapor condensation [3] or chemical vapor reaction [4]. In addition, plasma pyrolysis [5, 6, 7, 8] or laser ablation processes have been investigated [9, 10, 11, 12]. Another method for the fabrication of nanoparticles are precipitation processes from homogeneous solutions as a typical chemical bottom-up process. Chemical precipitation processes are well established for the fabrication of a huge variety of materials. The process, in general, is initiated by a nucleation step followed by a growth reaction [13, 14]. If the precipitation is carried out in very diluted solutions, as shown by Matievic [15], small particles in the nano range can also be produced by this route. One of the major drawbacks of the wet chemical process is that almost all precipitates show a rather high surface reactivity, mainly caused by residual surface groups, such as metal ion bonded OH groups or others. Due to their high surface small nano scaled particles generally show a strong interaction. If the particle size, as a result of the growth process, reaches the μm - or the $10\text{-}\mu\text{m}$ state, weak agglomerates can be separated by mechanical forces like milling or grinding. Usually, this is not possible in the nano range, which means that nanoparticles after precipitation have to be protected on their surface in order to avoid agglomeration. The simplest way of protecting them from approaching each other is to use electric charges, e.g. by establishing an appropriate pH value. The use of electric charge stabilization is the typical method applied by the so-called classical sol-gel process, which means that the fabrication of stable sols is generally carried out by this mechanism [16]. The aim of this paper is to show how the use of a surface modifier during the production process leads to agglomerate-free redispersible powders even through a continuous flow chemical process, and how a broad sintering regime is observed.

CERAMIC ASPECTS

Surface charge stabilized sols have been used for the fabrication of thin coatings, mainly on glasses. Due to the small particle size of the sols, which is in the lower nm range [17], transparent coatings can be obtained. SiO_2 and other inorganic coatings have been focused upon by numerous authors, especially for coatings on glass. Despite widespread activities in research, only a few industrial processes related to investigations have been developed so far. The fabrication of monolithic ceramics using sols has been investigated, but monolithic processing was rather unsuccessful because the fabrication of large-scale solids from sols is suffering from low solid content gels and green body gels which, due to their weakness combined with high shrinkage rates, are extremely difficult to be dried. The solidification of sols to gels is the crucial point in sol-gel nanotechnology. If the electric charges in electrostatically stabilized sols are 'removed', a very fast gelation process takes place with uncontrolled interaction between the sol particles, leading to a high concentration of defects and pores with a broad size distribution. This in turn leads to inhomogeneous sintering, and large pores can be closed only at higher temperatures. So the benefits of the nanoparticles cannot be exploited in the monolithic ceramic sol-gel processing and an undesired broad sintering range is obtained. This is schematically shown in fig. 1.

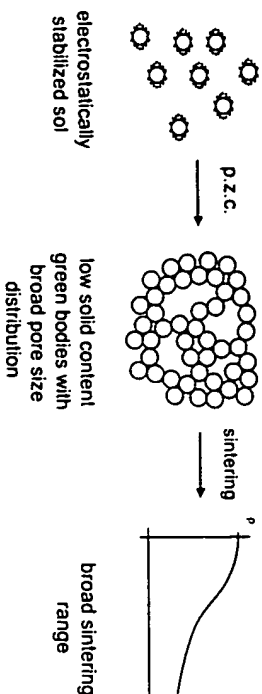


Fig. 1: Scheme of the typical sol-gel nanoparticle processing to parts.

Based on these considerations, alternative concepts have been developed for substituting electric charge stabilization by surface modification, as described in [18, 19, 20]. If molecules containing small functional groups are used to block the surface during or after the growth process, particle size, particle size distribution and particle interaction can be controlled easily. Moreover, if these small molecules are bifunctional, specific 'chemical reactivities' can be bonded to the particles' surface, influencing its chemical reactivity, its ζ -potential and, of course, its further processing properties. This is schematically shown in fig. 2.

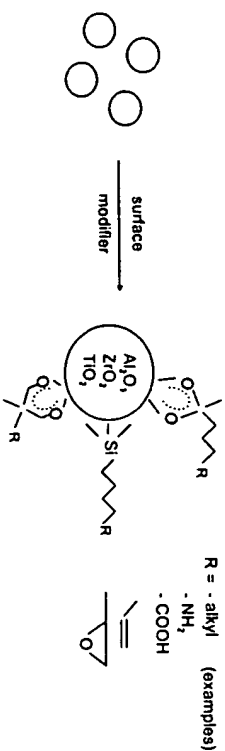


Fig. 2: Basic principle of a surface modification; examples for modification.

Relatively small molecules have to be used if the organic content of these systems shall be low, which might be of importance if ceramic processing is envisaged. This, in general, forbids the use of polyelectrolytes for stabilization, which are widely used in ceramic processing for powders with particle sizes in the μm range. The advantage, however, of surface modifiers of the polymer type is their perfect bonding to many inorganic surfaces. In order to keep the modifying molecules on the surface, specific bonds to the surface have to be used, but, as shown elsewhere [19], the chemical bond principle known from solution chemistry (salt and complex formation) can be used on the nanoparticles' surface. This means that a wide variety of monomeric, oligomeric and polymeric modifying components are available for the surface modification of nanoparticles. An interesting method may be the perfect surface coverage of oligomeric systems with the low organic content of small molecules. In this case, an exchange has to be carried out during processing.

For the preparation of larger amounts of surface stabilized powders, other aspects have to be taken into consideration, for example, the fabrication of well-crystallized particles, which normally is not the case in a complete way if one considers classical sols (alumina, titania or zirconia), which, in general, are only partly crystallized after fabrication. Other aspects are cleaning processes, separation processes and drying techniques to avoid agglomeration. In this paper, a route is described to prepare ceramic nanopowders by using different types of surface modifiers to obtain well-crystallized powders.

EXPERIMENTAL

Powder synthesis

$(\text{Y}_2\text{O}_3)/\text{ZrO}_2$
For the fabrication of zirconia powders, 255 g Zirconium-n-propoxide were dissolved in 200 ml of ethanol. This solution was slowly added to 200 ml of an aqueous solution of 7.6 g oleic acid polyethylenoxide ester ($(\text{CH}_3(\text{CH}_2)_9\text{CH}=\text{CH}(\text{CH}_2)_9\text{CO}_2(\text{CH}_2)_9\text{O})_n$, OPE), and 20 ml of 25 wt.% aqueous ammonia solution were added to establish a pH value of 11. For Y containing systems, $\text{Y}(\text{NO}_3)_3$ was added to the ethanol solution. The sol formation was completed after stirring for 3 h at 20 °C. The prepared sol was placed into an autoclave and was treated at 230 °C and 70 bar for 3 h. Afterwards, the suspension was flocculated by pH adjusting to pH = 5.9 with 20 ml of 1 N HCl, the point of zero charge of the prepared, modified particles and the solid was separated by filtration. In order to remove soluble reaction products, the resulting sediment was repeatedly diluted with 1 l of deionized water, flocculated by pH-adjusting to pH = 5.9 and again filtrated until the conductivity of the washing water was below 5 μS . Finally the powder was dried at 60 °C and 20 mbar.

$\text{SnO}_2/\text{Sb}_2\text{O}_3$
81.25 g of SnCl_4 * 5 H_2O and 2.66 g SbCl_3 (5 mole % with respect to Sn) were dissolved in 200 ml of ethanol. This solution was slowly added to 200 ml of an aqueous solution of 3.5 g OPE and 35 ml of aqueous ammonia (25 wt.%), the pH was 14. After stirring for 3 h at 20 °C, the resulting sol was hydrothermally treated at 150 °C and 10 bar for 3 h. The resulting reaction product was treated as described above.

$\text{SnO}_2/\text{In}_2\text{O}_3$
110 g of InCl_3 and 14.1 g SnCl_4 * 5 H_2O (8 mole % with respect to In) were dissolved in 250 ml of deionized water and then slowly added to 200 ml of an aqueous solution of 7 g OPE 35 ml of aqueous ammonia (25 wt.%), the pH was 14. The sol formation was completed after stirring for 5 h at 20 °C. After hydrothermal treating at 360 °C and 160 bar for 5 h crystallinity was achieved. The resulting reaction product was treated as described above.

Exchange of the Surface Modifier

In order to exchange the OPE bound on the particles' surface, 50 g of the powders were suspended in 200 ml of 8 n NaOH and 200 ml toluene were added and stirred for 5 h to extract hydrophobic reaction products. The mixture was heated under reflux for 5 h ('deesterification'). After the deesterification the solid was separated after the pH value of the aqueous suspension was adjusted to pH = 7 to flocculate the precipitate (point of zero charge of ZrO_2) by centrifugation (4000 r/min, 15 min). In order to remove soluble reaction products, the resulting sediment was repeatedly diluted with 1 l of deionized water, filtrated and washed until the conductivity of the washing water was below 5 μS . 4 g of nitroacetic acid (TODS) were added to the resulting suspension as surface modifier. After stirring for additional 3 h the pH of the suspension was adjusted to pH = 8 (point of zero charge of the TODS-modified ZrO_2) and the flocculated powders were washed as described above in order to remove excess TODS not bound onto the particles' surface. Finally, the powder was isolated by filtration and dried (60 °C, 20 mbar, 5 h). The synthesized powders were characterized by HRTEM, x-Ray, IR spectroscopy, and laser backscattering. ζ -potential measurements were carried out in aqueous suspensions (solid content: 1 wt.-%) by titration with 0.1 n NaOH and 0.1 n HCl, respectively.

RESULTS

In order to avoid agglomeration during the precipitation of nano-scale modified ZrO_2 particles the reaction was carried out in presence of the surface modifying agent OPE as described above. This molecule is rather large, but it has been selected because of its ability to prevent agglomeration. For further processing to ceramics, the organic content is too high, so a second step to remove the ester has to be taken into consideration. The precipitates were analyzed by X-ray diffraction, TEM, IR spectroscopy, and the particle size distributions were also measured. As shown in fig. 3a, the particles are rather amorphous after precipitation. From TEM investigations, not shown here, the size of the amorphous precipitates can be roughly estimated to be in the range of 5 - 10 nm. The particles can easily be dispersed in water at pH 8 and the size distribution is shown in figure 3b. The particle size is in the nm range with a narrow distribution where 90 % of the particles are smaller than 30 nm.

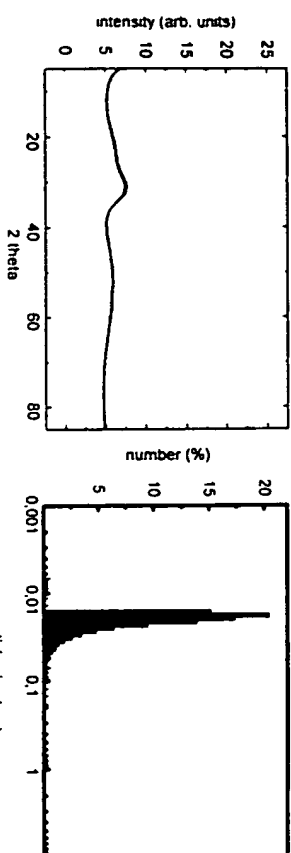


Fig. 3a: X-ray diffraction patterns of ZrO_2 nanoparticles coated with OPE after precipitation.

Fig. 3b: Laser backscattering measurement of the distribution of ZrO_2 nanoparticles coated with OPE in H_2O as solvent at pH = 8.

In order to obtain a better crystallinity, a solvo-thermal treatment seemed to be an interesting option. It is a well-known fact that inorganic precipitates can be recrystallized under hydrothermal conditions (mixture of EtOH and H_2O). The interesting question here was how far the OPE survives the solvo-thermal process and to what extent it maintains its protective function during this solvo-thermal process. For this reason, an IR spectrum was taken from the powder covered with about 10 wt.-% of the OPE before the treatment (fig. 4).

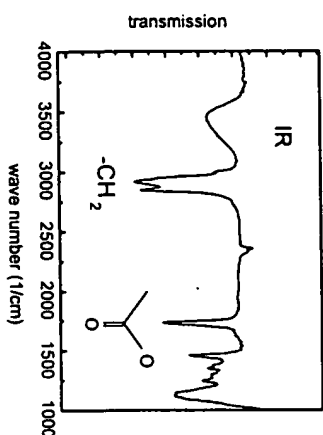


Fig. 4: IR-spectrum of ZrO_2 nanoparticles coated with OPE as received after precipitation.

The carboxylic frequency of the ester can be easily identified. After the hydrothermal treatment, the X-ray diffraction pattern of the zirconia containing 8 % of yttria (fig. 5) clearly shows the cubic modification, which can be attributed to the solvo-thermal treatment.

The IR spectrum of the washed powder (fig. 6) shows that the ester on the zirconia particle remains completely unchanged. As well as by laser backscattering (fig. 8). This means that first, the selected OPE survives the solvo-thermal process without decay and second, that the particle size remains almost unchanged, meaning that no agglomeration or detectable grain growth has taken place.

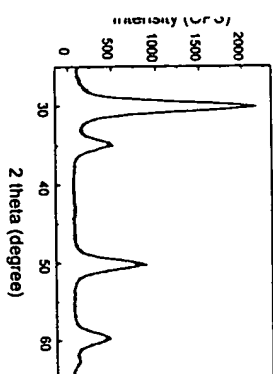


Fig. 5: X-ray diffraction spectrum of Y_2O_3/ZrO_2 after hydrothermal crystallization (230 °C, 70 bar, 3 h).

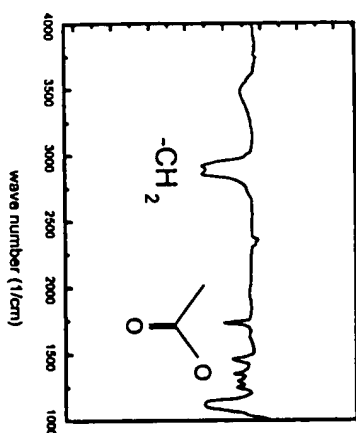


Fig. 6: IR-spectrum of the washed ZrO_2 nanoparticles coated with OPE after hydrothermal crystallization at 230 °C, 70 bar, 3 h.

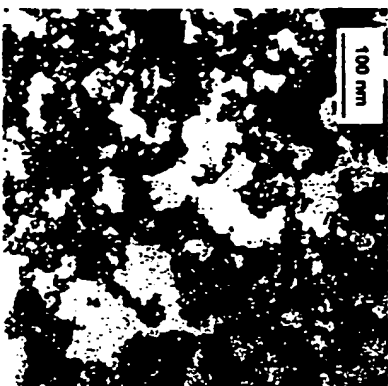


Fig. 7: HRTEM micrograph of 8-Y₂O₃/ZrO₂ after hydrothermal crystallization (230 °C, 70 bar, 3 h), surface modifier: OPE.

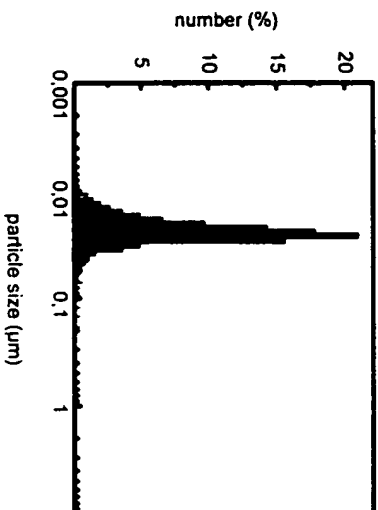


Fig. 8: Laser backscattering measurement of the distribution of crystallized and washed ZrO₂ nanoparticles coated with OPE in H₂O as solvent at pH = 3.

Different techniques were investigated to substitute the polymeric ester. The direct treatment of the ester-coated particles with short-chain molecules like β -diketones or carboxylic acids, was unsuccessful. This is due to the strong bond of the polymeric ester to the particle surface. The treatment of the system with sodium hydroxide, however, led to a complete removal of OPE from the surface. After the NaOH treatment, precipitating the nanoparticles by flocculation at the point of zero charge and washing the system to neutral, the addition of carboxylic acids led to a short-chain molecular coating. In fig. 9 the ζ -potential curves of the zirconia particles covered with OPE, the zirconia particles after NaOH treatment and washing to neutral as well as after recoating them with trioxadecanoic acid (TODS) are shown. The ζ -potential curves show clearly the effect of the different reaction steps. Flocculation of the uncoated ZrO₂ takes place at the point of zero charge close to pH7.

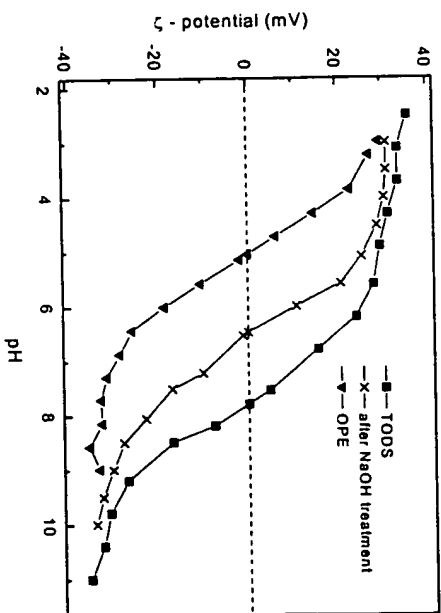


Fig. 9: pH-dependent ζ -potential of hydrothermally crystallized ZrO₂.

i.e. for the NaOH treated and washed precipitates, which can easily be filtered. Flocculation is a step considerably facilitating the separation; otherwise it is extremely difficult to separate nanoparticles from liquids. After drying, these powders are very well redispersible in water, as described elsewhere [19]. In fig. 10 the IR spectrum of the TODS modified yttria/zirconia is shown. It clearly depicts the C=O frequency of a carboxylate group and not the frequency of the free carboxylic acid. That means that the acid group is bonded to the particle

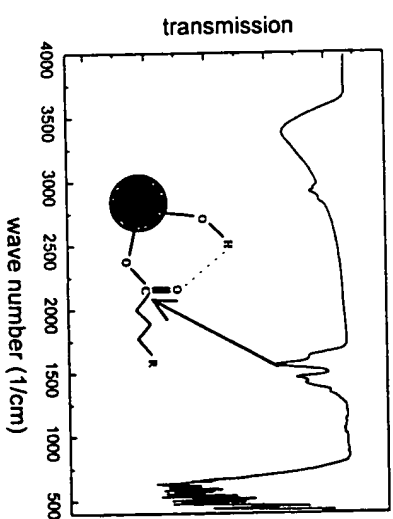


Fig. 10: IR-spectrum of the TODS-modified Y₂O₃/ZrO₂.

surface. Analytical investigations show that on the average 400 molecules of TODS are absorbed per particle. This leads to a total organic content of about 7.7 wt.-%. Up to now, it has not yet been clearly known why powders modified OPE are less redispersible than the TODS systems.

Based on these investigations, a concept of a process has been worked out, the flow chart of which is shown in fig. 11.

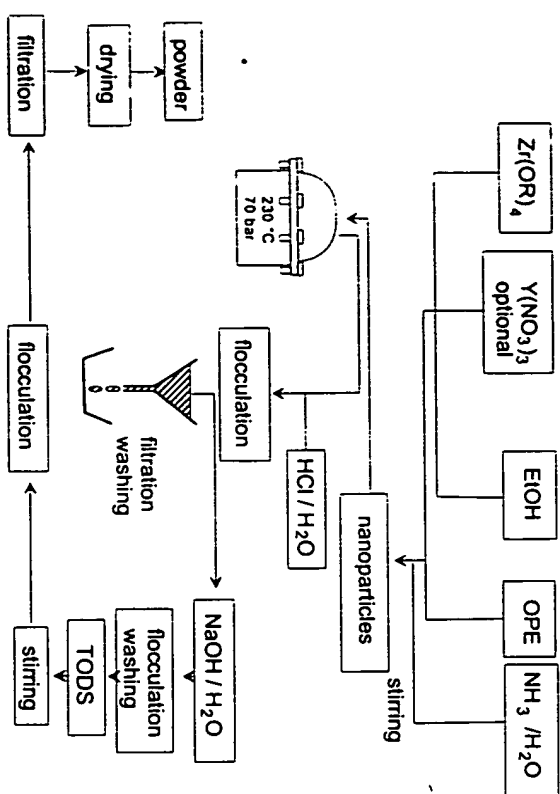


Fig. 11: Flow chart of the process.

All steps of this process consist basically of well-known chemical processing technologies and what seems to be important is that after the autoclave reaction, a water based technology is used. A chemical engineering development has been carried out to change the batch reactor system into a continuous flow reactor system for continuous nanopowder production. In fig. 12, the scheme of the production line is shown. The core technology part of the system includes a continuous flow hydrothermal reactor tube. This technique has been built up for pilot scale production of zirconia or zirconia/yttria powders at first and was then used for other systems, too. The system consists of several precursor containers (closed system technology). For sensitive systems, the reactions can be carried out under inert gas conditions. The liquids are pumped into the reaction container, stirred for the requested time period and then pumped into the storage container. From the storage container the liquid pumped into a heater where it is heated up to (2) the desired temperature and then pumped continuously into the tube reactor (3). The flow rate is adapted to the requested retention time. In (3) the treated liquid is cooled down, the pressure is relaxed and the flocculation, filtration and the surface modification steps are carried out.

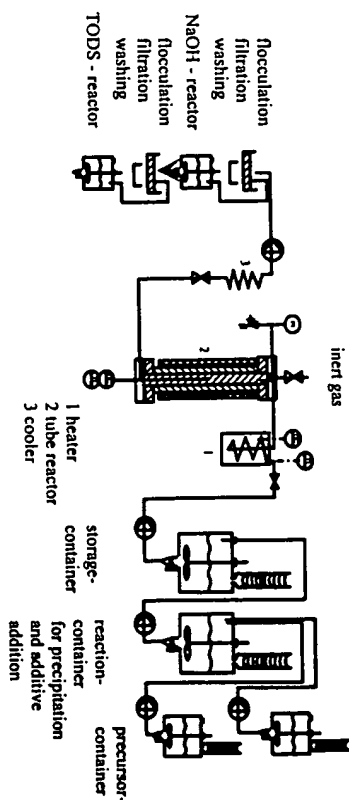


Fig. 12: Flow chart of the continuous flow reactor for the hydrothermal crystallization of nanocrystalline powders in solution [21].

The fabrication of antimony and indium doped tin oxide (ATO or ITO) powders is basically carried out by using the same reaction principles. In fig. 13 the flow chart for the synthesis of ATO or ITO particles is shown.

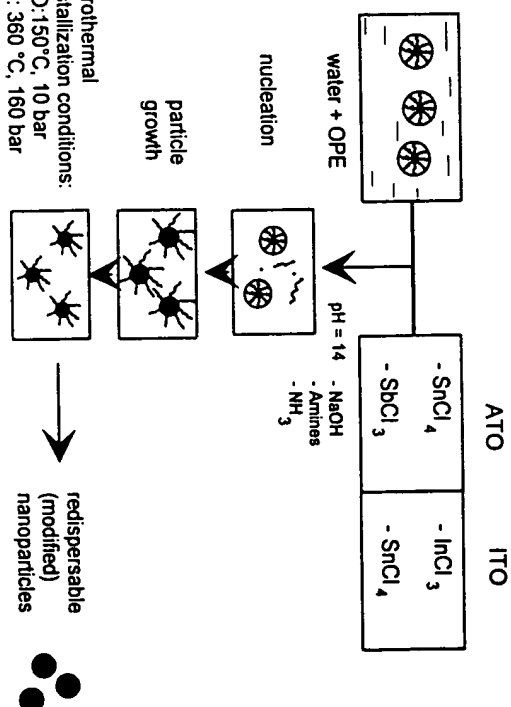


Fig. 13: Flow chart for the preparation of nanocrystalline ATO- and ITO particles.

Only the chlorides have been used as precursors. For both, ATO or ITO, identical processing parameters have been applied. The hydrothermal conditions in this case have been optimized to 150 °C and 10 bar for 4 hrs. In fig. 14 the X-ray diffraction patterns and the HRTEM micrograph of an ATO powder obtained by this process are shown. As can be recognized in the diffraction patterns, the particle size is rather small. In the high-resolution TEM, the particle size can be identified to be between 3 and 5 nm, which is in accordance with the particle size calculated from the diffraction patterns. No high temperature treatment has been carried out so

far with these powders in order to establish appropriate electronic properties. As in the case of ZrO_2 , ITO as well as ATO can be redispersed in H_2O to fabricate sols for optical purposes.

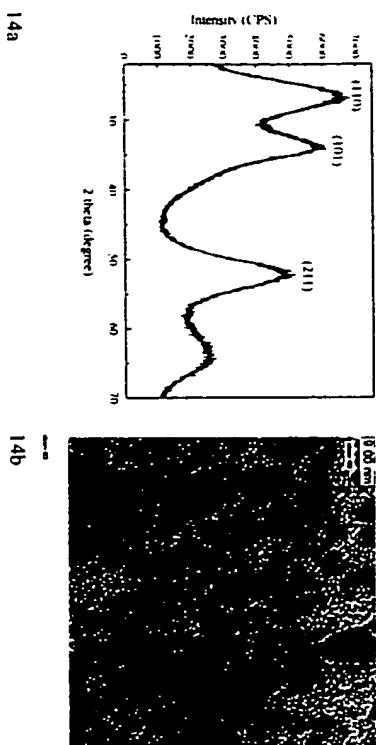


Fig. 14a: X-ray diffraction of nanocrystalline antimony-doped (5 mole %) tin dioxide. 14b: HRTEM picture of nanocrystalline powder dispersed in water and tetramethylammoniumhydroxide. Particle size ranges from 3 to 5 nm. The surface modifier chosen in this case was TODS.

As shown elsewhere [20], these powders can be used for green body fabrication with green densities up to 60 vol.-% with a mono modal pore size distribution in the nm range. $Y-ZrO_2$ has been densified to full density at temperatures below 1100 °C and due to the narrow pore size distribution very narrow sintering range has also been obtained. This shows the potential of these powders for ceramic processing.

CONCLUSION

The investigations of using a combination of controlled growth precipitation reactions in the presence of surface modifiers, the solvo-thermal treatment for achieving desired crystallinity and the exchange of ligands in order to obtain suitable processing properties have shown that it is possible to synthesize agglomerate-free well crystallized nanoparticulate powders.

This process can be used for nanoparticle fabrication of various compositions. The use of oligomeric molecules leads to a perfect protection during the precipitation as well as during the solvo-thermal crystallization. This protection is necessary in order to maintain the particle size distribution obtained from the precipitation process. For further processing of the nanoparticles the relatively high amount of organics introduced into the system by the oligomeric compounds may be disturbing. For this reason, it is necessary to remove the genuine coating first by substituting it in a two step chemical process through an electrostatic stabilization (for example, the absorption of sodium ions, protons or others) and then to recast them with short-chain molecules of the desired type, e.g., carboxylic acids. The carboxylic acid coatings lead to systems that are completely redispersible in water. These nanoparticulate systems can be then used for many purposes, for example for ceramic processing or for coatings, even optical coatings, since the particle size is very small. The advantage compared to conventional sol-gel processing is that the systems can easily be stored in form of dry powders, which is very convenient compared to sol storage. In addition to this, water-based technologies can be used very easily compared to the alcohol-based technologies in the conventional sol-gel processes.

Last but not least, the technology is based on well known chemical engineering processes with the potential to build up continuous flow low cost productions.

ACKNOWLEDGMENT

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US005246624A

United States Patent [19]

Miller et al.

[11] Patent Number: **5,246,624**[45] Date of Patent: **Sep. 21, 1993**[54] **AQUEOUS COLLOIDAL DISPERSION OF FUMED SILICA, ACID AND STABILIZER**[75] Inventors: **Dennis G. Miller, Urbana; William F. Moll, Crystal Lake, both of Ill.**[73] Assignee: **Cabot Corporation, Boston, Mass.**[21] Appl. No.: **829,609**[22] Filed: **Jan. 30, 1992****Related U.S. Application Data**

[63] Continuation of Ser. No. 326,890, Mar. 21, 1989, abandoned.

[51] Int. Cl.⁵ **B01J 13/00; C01B 33/14**[52] U.S. Cl. **252/313.2; 252/310; 106/287.34; 423/336; 51/308**[58] Field of Search **252/310, 313.2; 106/287.34; 65/901; 51/308; 423/336**[56] **References Cited****U.S. PATENT DOCUMENTS**

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An aqueous colloidal dispersion of fumed silica, acid and stabilizer, having a fumed silica concentration of at least about 40% by weight. A process for making an aqueous colloidal dispersion is also disclosed.

21 Claims, No Drawings

means that the dispersion will not gel for a period of at least 1 day. Typically, the aqueous colloidal dispersions of fumed silica produced according to the process of the present invention are stable for a period of at least a week, preferably several weeks, and more preferably several months to years. As previously explained, for the purposes of the present invention "non-dilatant" refers to the ability of a dispersion to pass through a 1000 micron or smaller pore size filter without gelling. Typically the aqueous colloidal dispersions of fumed silica, produced according to the process of the present invention, will pass through a 250 micron or smaller pore size filter, preferably through a 25 micron or smaller pore size filter, and more preferably through a 10 micron or smaller pore size filter. Typically the "low viscosity" of the aqueous colloidal dispersions of fumed silica, produced according to the process of the present invention, will be below about 1000 centipoise, preferably below about 250 centipoise.

Another advantage of the present invention is that the aqueous colloidal dispersions of fumed silica, acid and stabilizer, having a fumed silica concentration of at least about 40%, by weight, are stable for a period of months to years, have low viscosities and are non-dilatant. The low viscosity and non-dilatant qualities permit the aqueous colloidal dispersion to pass through a fine filter.

Additional advantages of the present invention will become apparent from the following more detailed description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

According to the present invention a mixer is charged, generally up to about 50%, with a quantity of water, preferably water which has been de-ionized, and acid is added to the water. Preferably the mixer utilized is a high shear mixer, capable of forming the dispersions, such as those generally known to the art. The acid may be a mineral or organic acid such as hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, acetic acid or maleic acid. The quantity of acid added to the water is based on the amount of fumed silica which will be added to the water to form the final aqueous colloidal dispersion. Generally the quantity of acid added to the water is an amount, by weight, between about 0.0025% and about 0.50%, and preferably between about 0.02% and 0.15% of the amount, by weight, of fumed silica which will be added to the water. After the addition of acid to the water the mixer may be operated to mix the acid and water to form a water-acid solution.

The percentage water initially charged to the mixer can obviously vary. However, as will become apparent from the following description, there must be room left in the mixer to add fumed silica and additional water. The initial quantity of water chosen is usually based on the amount of fumed silica to be added, and the desired final concentration of fumed silica in the aqueous colloidal dispersion. For example, if the desired final concentration of the aqueous colloidal dispersion of fumed silica is about 50% fumed silica, by weight, and 100 lbs. of fumed silica are to be added to the mixer, then the initial quantity of water is that quantity which will result in a greater than 50% by weight concentration of fumed silica in the mixer. Typically, in the process of the present invention the dispersion in the mixer, before dilution, will have a fumed silica concentration at least about 5% greater than the desired final concentration of

fumed silica in the aqueous colloidal dispersion of fumed silica. Thereafter the aqueous colloidal dispersion in the mixer will be diluted by the addition of an additional amount of water to achieve the desired final concentration of fumed silica in the dispersion of about 50% by weight.

After the mixer is charged with water, and acid is added to the water, fumed silica is added to the water-acid solution in the mixer. The fumed silica may be added by mixing the fumed silica into the water-acid mixture while the mixer is operating, or by adding the fumed silica to the water-acid mixture and then operating the mixer. The fumed silica may also be added incrementally, in a series of steps, with the mixer operating between each step.

As previously discussed the process of the present invention may be utilized with fumed silicas having any surface areas. To produce aqueous colloidal dispersions of fumed silica having fumed silica concentrations at least about 40% by weight, preferably a fumed silica with a surface area less than about 75 sq.m/g is utilized. More preferably a fumed silica with a surface area between about 10 sq.m/g and about 75 sq.m/g is utilized, and most preferably a fumed silica with a surface area between about 35 sq.m/g and about 60 sq.m/g is utilized to form the aqueous colloidal dispersions of fumed silica having fumed silica concentrations of at least about 40% by weight.

The immediate effect of the addition, or each addition, of fumed silica to the mixer will be to thicken the aqueous colloidal dispersion of fumed silica in the mixer. As the mixer continues to operate however, the aqueous colloidal dispersion of fumed silica in the mixer will thin.

After the concentration of fumed silica, by weight, in the aqueous colloidal dispersion of fumed silica in the mixer has been raised to a point above the desired final concentration of fumed silica, by weight, the mixer is allowed to operate until the dispersion in the mixer thins. As previously explained, typically in the process of the present invention, the dispersion in the mixer, before dilution, will have a fumed silica concentration at least about 5% greater than the desired final concentration of fumed silica in the aqueous colloidal dispersion of fumed silica. Then an additional amount of water is added to the mixer to dilute the dispersion in the mixer. Preferably this additional water has been deionized. The additional water is then mixed into the aqueous colloidal dispersion in the mixer by operating the mixer. The amount of water added is the amount which will lower the concentration of fumed silica, by weight, of the aqueous colloidal dispersion of fumed silica in the mixer to the desired final concentration, taking into account the stabilizer which will be added to the dispersion.

After the additional water has been added, a stabilizer, such as an alkali or amine, is added to the aqueous colloidal dispersion of fumed silica in an amount which will adjust the pH of the final dispersion to between about 7 and about 12, preferably between about 7.5 and about 11. The particular pH chosen for the final dispersion will depend on the application for which the aqueous colloidal dispersion of fumed silica is designed. Suitable stabilizers include, but are not limited to, alkalis or amines such as sodium hydroxide, potassium hydroxide, lithium hydroxide, ammonium hydroxide, triethylamine, and dimethylethanol amine.

dispersing fumed silica into said preacidified volume of water in an amount at least sufficient to provide said preselected concentration and under sufficiently high shear mixing conditions as to form an acidic aqueous colloidal dispersion of said silica; mixing a pH raising stabilizer into said acidic aqueous colloidal dispersion of said silica in an amount sufficient to being the pH of the dispersion to between about 7.0 and about 12.0; and collecting the resulting stabilized aqueous colloidal fumed silica dispersion as product; wherein the dispersion will not gel for a period of at least 1 day, has a viscosity of below about 1000 centipoise, and is non-dilatant.

2. The colloidal dispersion product of claim 1 wherein the fumed silica is present in an amount between about 40% and 65% by weight.

3. The colloidal dispersion product of claim 1 wherein the fumed silica is present in an amount of about 40% by weight.

4. The colloidal dispersion product of claim 1 wherein the fumed silica is present in an amount of about 45% by weight.

5. The colloidal dispersion product of claim 1 wherein the fumed silica is present in an amount of about 50% by weight.

6. The colloidal dispersion product of claim 1 wherein the fumed silica is present in an amount of about 55% by weight.

7. The colloidal dispersion product of claim 1 wherein the fumed silica is present in an amount of about 60% by weight.

8. The colloidal dispersion product of claim 1 wherein the fumed silica is present in an amount of about 65% by weight.

9. The colloidal dispersion product of claim 1 wherein the acid is selected from the group consisting of mineral acids and organic acids.

10. The colloidal dispersion product of claim 1 wherein the acid is selected from the group consisting

of hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, acetic acid and maleic acid.

11. The colloidal dispersion product of claim 1 wherein the acid is hydrochloric acid.

12. The colloidal dispersion product of claim 1 wherein the acid is present in an amount between 0.02% and about 0.15% of the amount by weight of the fumed silica.

13. The colloidal dispersion product of claim 1 wherein the acid is selected from the group consisting of alkalis and amines.

14. The colloidal dispersion product of claim 1 wherein the acid is selected from the group consisting of sodium hydroxide, potassium hydroxide, lithium hydroxide, ammonium hydroxide, triethylamine, and dimethylethanol amine.

15. The colloidal dispersion product of claim 1 wherein the stabilizer is ammonium hydroxide.

16. The colloidal dispersion product of claim 11 wherein the stabilizer is ammonium hydroxide.

17. The colloidal dispersion product of claim 1 wherein the stabilizer is added in an amount which raises the pH of the dispersion to between about 7.5 to about 11.

18. The colloidal dispersion product of claim 1 wherein the fumed silica has a surface area less than about 75 sq.m/g.

19. The colloidal dispersion product of claim 1 wherein the fumed silica has a surface area between about 10 sq.m/g and about 75 sq.m/g.

20. The colloidal dispersion product of claim 1 wherein the fumed silica has a surface area of about 50 sq.m/g.

21. The colloidal dispersion product of claim 1 wherein the amount of fumed silica dispersed in said volume of preacidified water in said dispersing step is at least about 5% greater than said preselected silica concentration of the final dispersion product and wherein, following said dispersing step and preceding said stabilizing step, sufficient additional water is mixed into said acidic colloidal dispersion to dilute same to said preselected silica concentration.

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United States Patent [19]

Chieng et al.

US005158758A

[11] Patent Number: 5,158,758

[45] Date of Patent: Oct. 27, 1992

[54] PRODUCTION OF SILICA HAVING HIGH SPECIFIC SURFACE AREA

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[21] Appl. No.: 342,547

[22] Filed: Apr. 24, 1989

[51] Int. Cl.³ C01B 33/14

[52] U.S. Cl. 423/338; 423/336

[58] Field of Search 423/336, 338, 341, 481; 65/18.1

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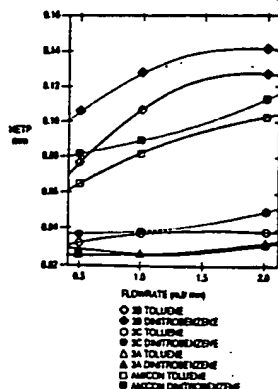
Attorney, Agent, or Firm—Wendall Ray Guffey; Thomas L. Farquer; William J. Fisher

[57]

ABSTRACT

A method for production of high specific surface area silica gel by hydrolysis of silicon tetrahalide, wherein a solution of silicon tetrahalide in a non-reactive solvent such as alcohol is mixed with water to produce silica gel having a high surface area and narrow pore diameter distribution especially suited for use as normal phase packing material in high performance chromatography columns. The water contains fluoride ions if the halide is chloride. Reverse phase packing material can be prepared by reacting the normal phase silica gel with organochlorosilanes to prepare bonded reverse phase material for use in high performance liquid chromatography systems.

20 Claims, 8 Drawing Sheets



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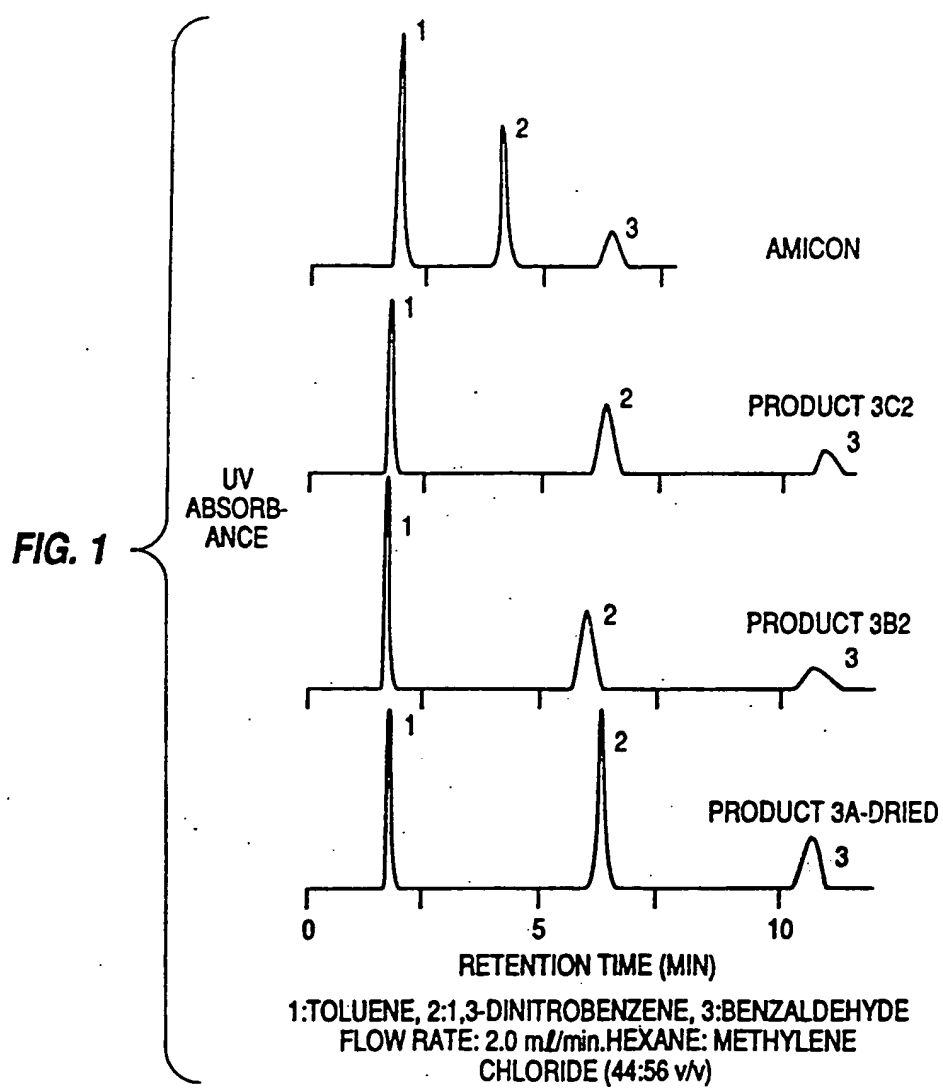
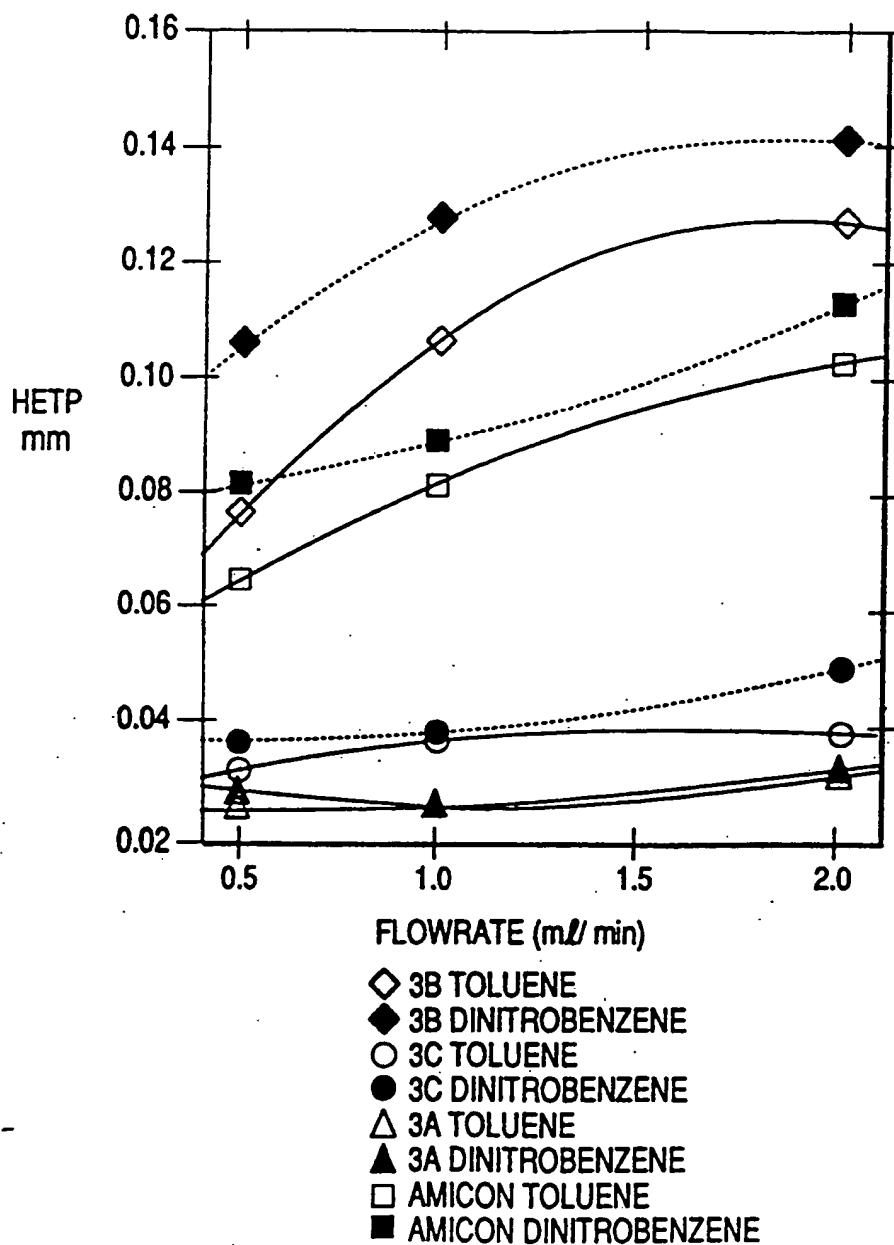
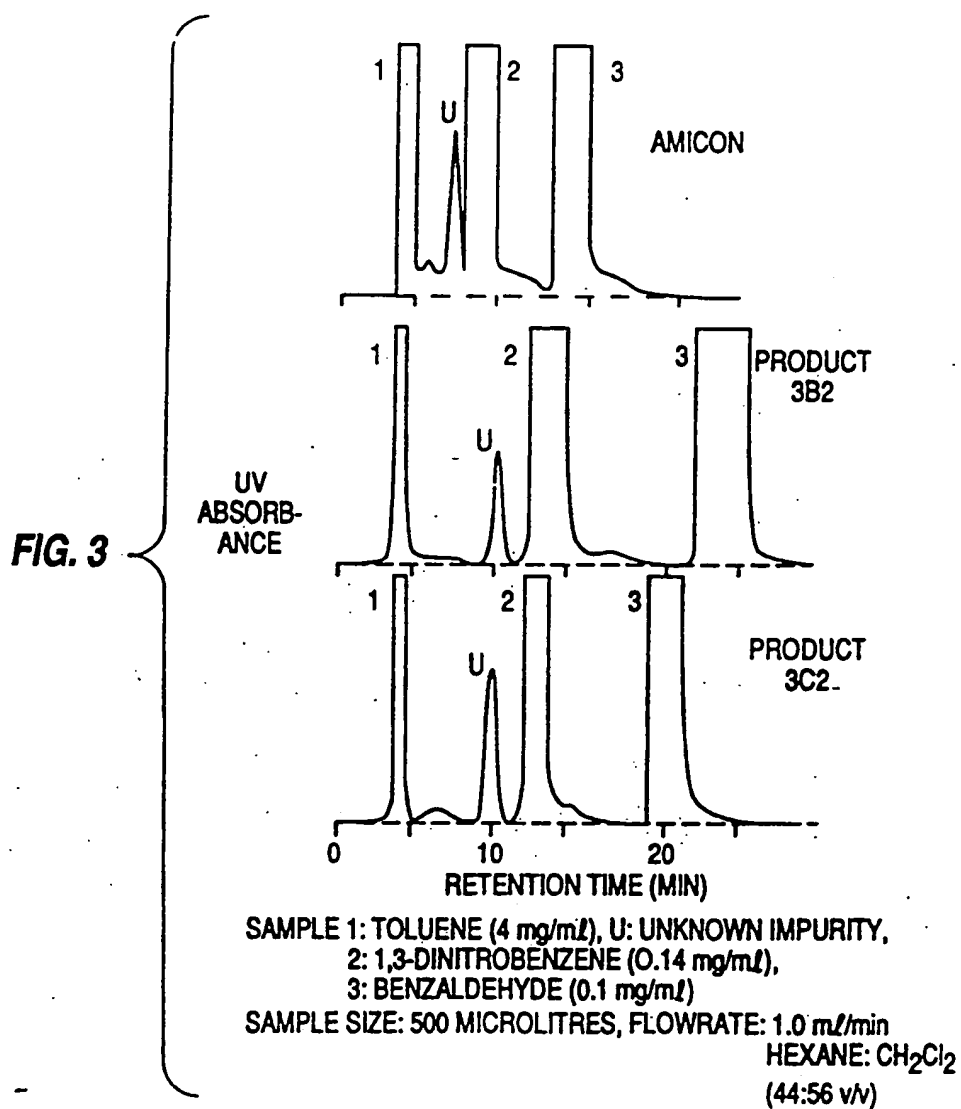
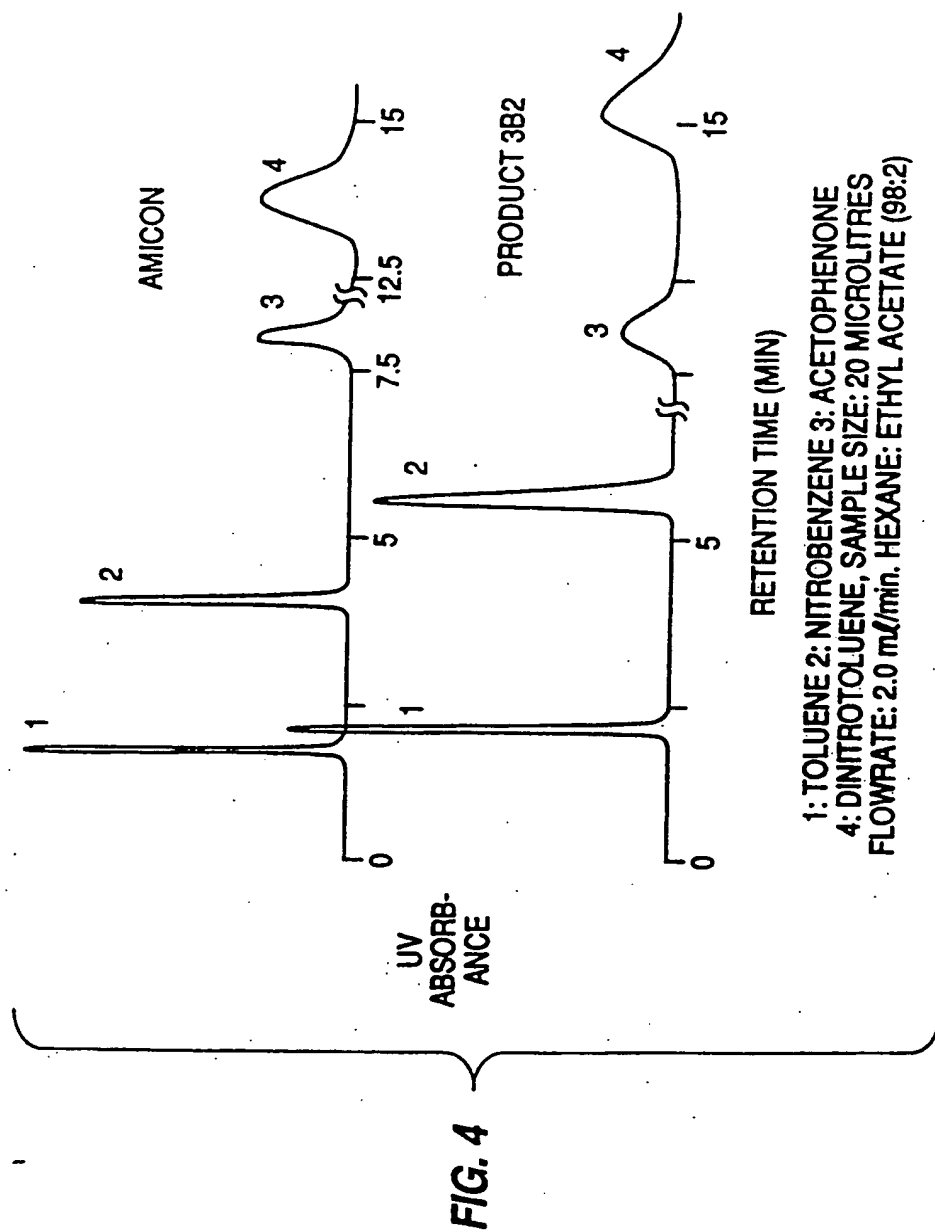
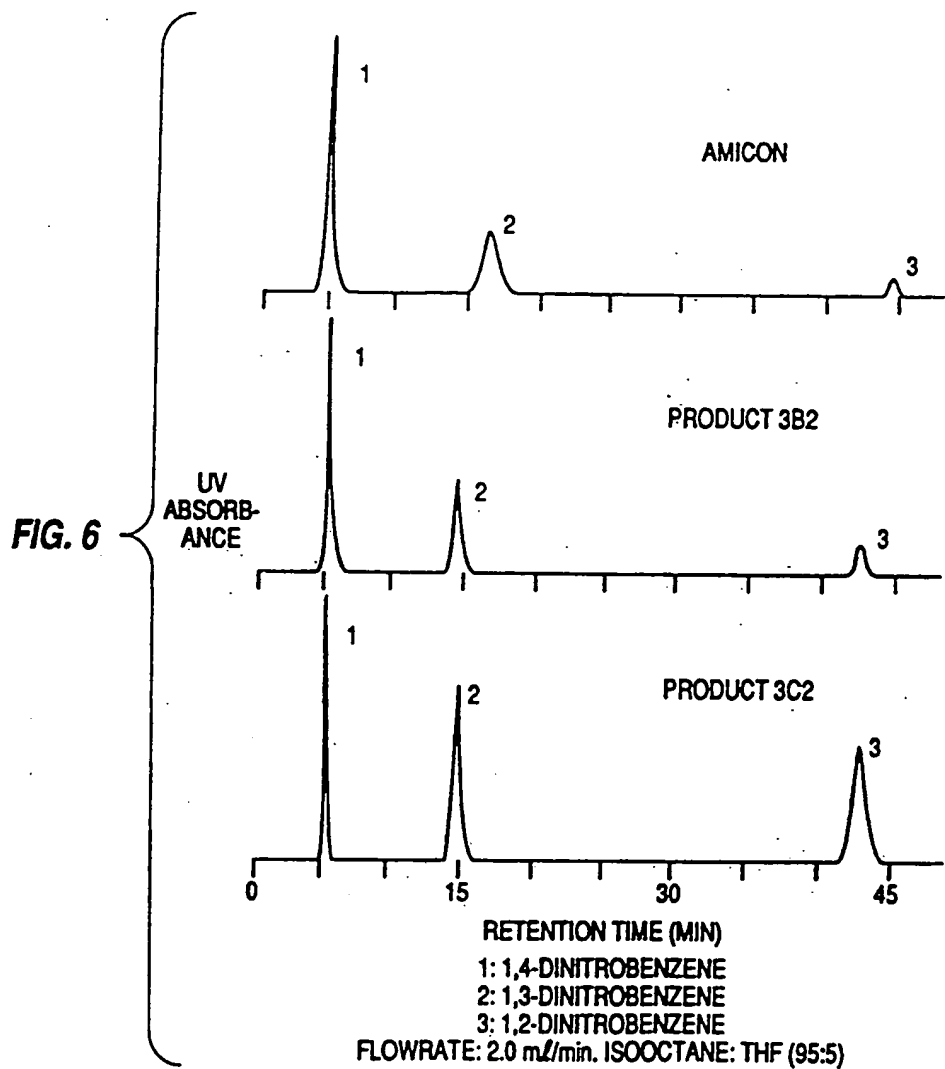


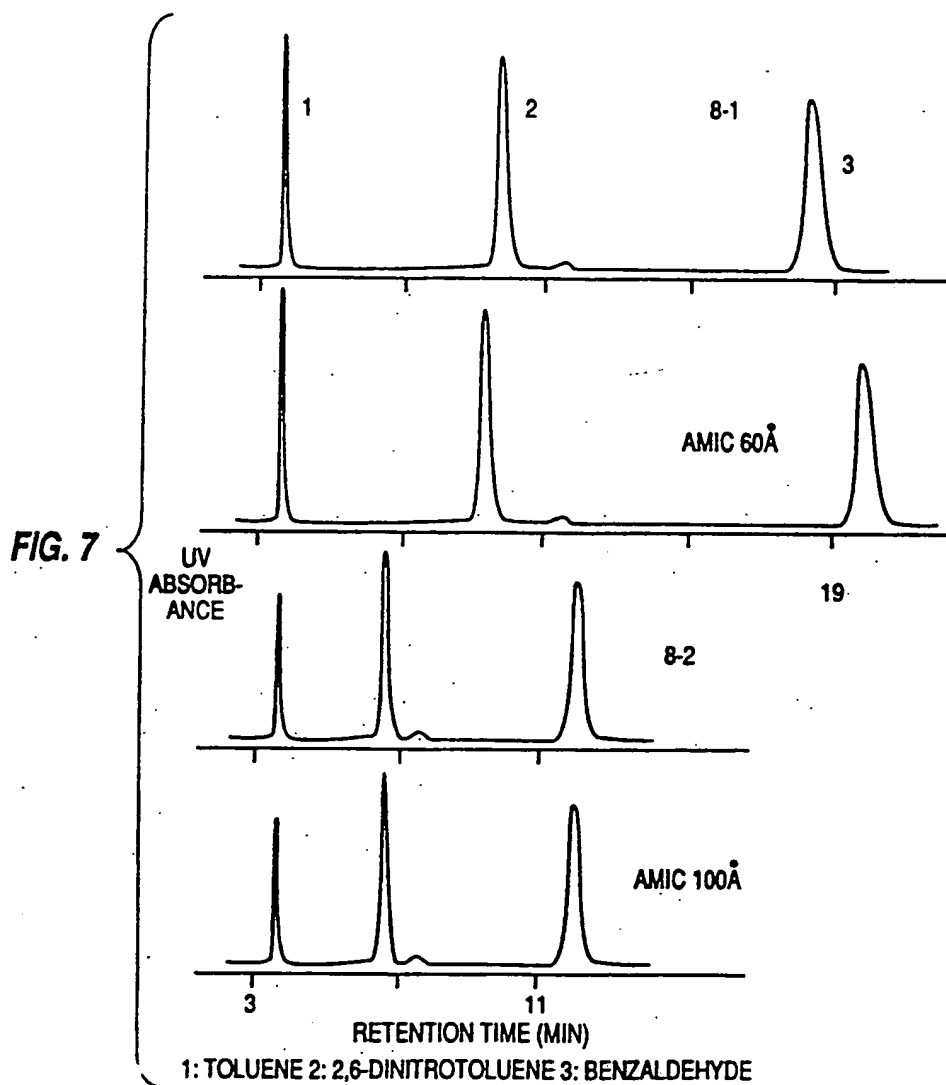
FIG. 2

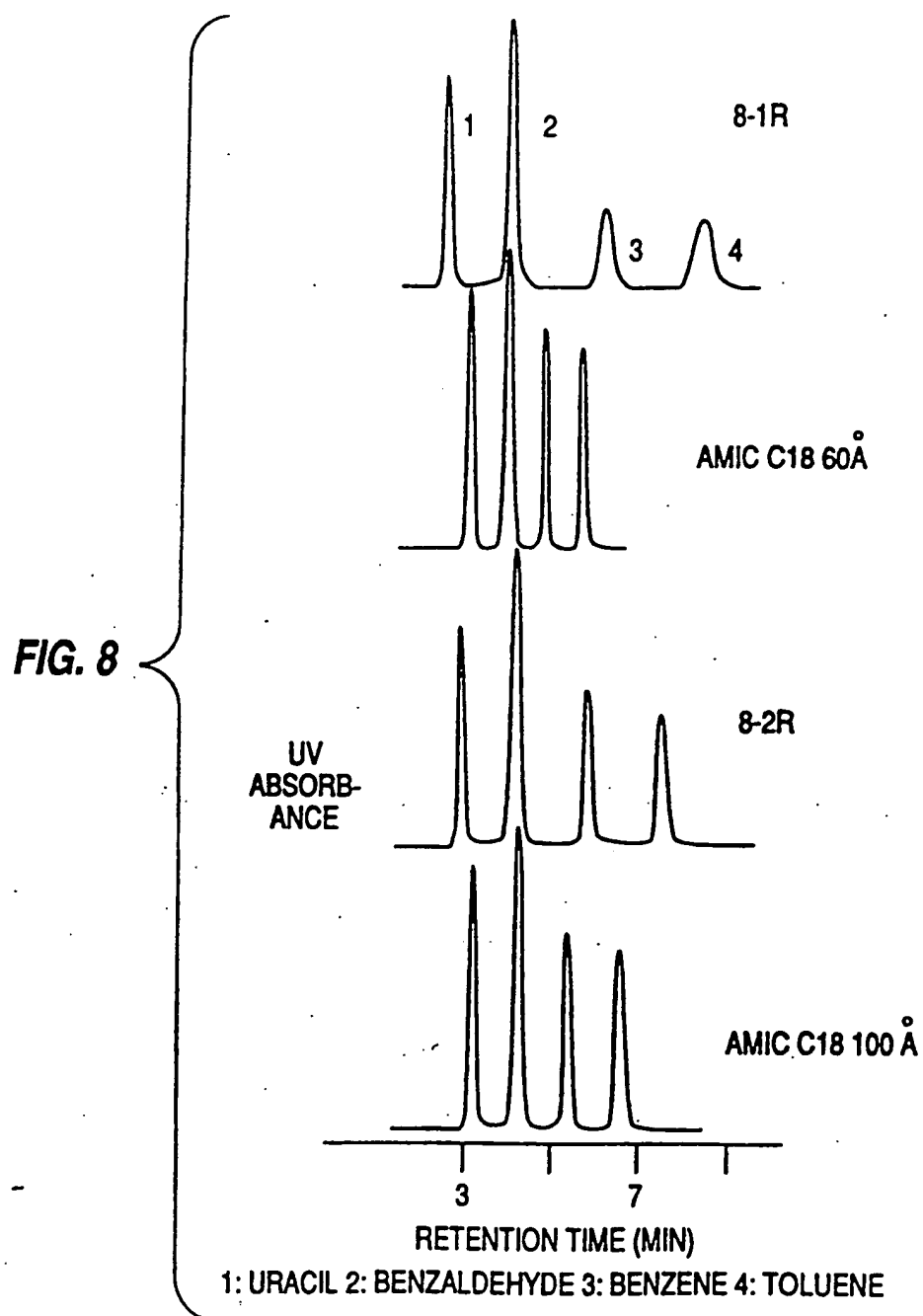












PRODUCTION OF SILICA HAVING HIGH SPECIFIC SURFACE AREA

BACKGROUND OF THE INVENTION

1. Field of The Invention

This invention relates to a method of producing high specific surface area silica (SiO_2) of uniform porosity suitable for liquid chromatography uses by hydrolysis of silicon tetrafluoride (SiF_4) or silicon tetrachloride (SiCl_4).

2. Description of Related Art

Silica gel is widely used in chromatographic separations. Silica gel having high specific surface area and uniform porosity is especially useful in chromatographic techniques. Because impurities interfere with chromatographic separations, suitable silica gel desirably is essentially pure. Suitable silica must also have high strength so that it is not crushed under high pressures utilized for high performance liquid chromatographic separations.

Silica gel used in chromatographic separations must have uniform properties, not only within one chromatography column, but also from column to column, to ensure reproducibility of results. Thus, it is not sufficient to have uniform properties merely within a single batch of silica gel. Properties of silica gel must be uniform and predictable from batch to batch. The cost must also be reasonable.

High specific surface area silica gel produced using known techniques is unsatisfactory in one or more of these aspects. For example, silica gel produced by hydrolysis of tetraethoxysilane (TEOS) is expensive because TEOS is a relatively expensive reactant. Acidulation of sodium silicate does not involve expensive starting materials, but produces a silica gel product which contains large quantities of contaminants such as unreacted silicates. The level of impurities is sufficient to make the silica gel unsuitable for use in chromatographic separations.

U.S. Pat. No. 3,236,594 discloses a process for making finely divided silica from silicon tetrafluoride. The process is operated at ordinary temperature and fluorine is recovered as an inorganic fluoride. Silicon tetrafluoride is absorbed into a lower aliphatic alcohol to form a solution of a stable complex. This solution is reacted with inorganic base chosen from the group consisting of ammonium hydroxide and the oxides and hydroxides of alkali metals and alkaline earth metals and at least a stoichiometric amount of water to hydrolyze the silicon tetrafluoride. Then, silica is separated from the mixture containing metal fluoride or ammonium fluoride. However, silica gel produced by this method is unsatisfactorily powdery and is not suitable for use in high performance liquid chromatography columns.

Liquid chromatography columns using silica gel typically are either normal phase or reversed phase. Normal phase liquid chromatographic separations utilize interactions between polar silanol moieties on the surface of the column packing and the composition being separated. In reversed phase liquid chromatography, a non-polar stationary phase is bonded to the silanol group on the surface of the silica gel. This stationary phase, in combination with terminal groups ("endcaps") reacted onto the stationary phase, interact with the composition being separated.

The properties of silica gel suitable for normal phase use, described above, are similarly desirable for silica

gel used as substrate for reverse phase liquid chromatography columns. However, additional characteristics are necessary for reverse phase liquid chromatography column packing. To ensure reproducibility of result, the stationary phase should be normally distributed, i.e., distributed in a monolayer, over the surface of the silica gel.

Various stationary phases have been bonded on the surface of silica gel particles. Octadecylchlorosilanes are often used as the stationary phase. Organochlorosilanes of other carbon numbers (e.g., C_2 , C_4 , and C_8) also are used for surface bonding. Use of monochlorosilane compounds typically ensures monolayer distribution of the stationary phase over the silica gel substrate.

The consistency of quality required of silica gel used in chromatographic columns requires control over product properties. It is difficult to control product characteristics, however, in known processes requiring gelation of silicon tetrachloride in which a large stoichiometric excess of water is used. Further, these processes require long gelling periods, and the specific surface area of silica thus produced is too high for chromatographic uses.

It is an object of this invention to provide a method for producing high specific surface area silica gel by hydrolysis of silicon tetrahalide, i.e., silicon tetrafluoride or silicon tetrachloride.

It is another object of the invention to provide a method for obtaining silica gel having a selected specific surface area and narrow pore diameter range.

It is a further object of this invention to provide a high specific surface area silica gel suitable for use in high performance liquid chromatography columns.

It is yet another object of this invention to provide a method of preparing material which can be bonded to prepare packing material for reversed phase high performance liquid chromatography columns.

SUMMARY OF THE INVENTION

In accordance with these and other objects, this invention relates to a method for production of high specific surface area silica of a uniform porosity gel by hydrolysis of silicon tetrahalide. According to the process, a solution of silicon tetrahalide in a non-aqueous solvent such as alcohol is mixed with water to produce silica gel having a very high surface area especially suited for use as normal phase packing material in high performance chromatography columns. In the case of silicon tetrachloride, fluoride ion also is present in the water. Reverse phase packing material can be prepared by reacting the normal phase silica gel with organochlorosilanes to prepare bonded reverse phase material for use in high performance liquid chromatography systems.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates the separation performance of silica gel columns.

FIG. 2 is the van Deemeter plots corresponding to the separations illustrated in FIG. 1.

FIGS. 3-8 illustrate various comparisons of separation performance.

DETAILS OF THE INVENTION

This invention is based on the discovery that silica gel produced by hydrolysis of silicon tetrahalide absorbed in a non-aqueous solvent such as alcohol has high spe-

sific surface area and a uniform porosity. Silica gels prepared by controlled hydrolysis have properties suitable for use as high performance liquid chromatography column packing. Reverse phase high performance liquid chromatography column packing material can be prepared by reacting this high surface area silica gel with organochlorosilanes and other bondable constituents.

Silica gel produced in accordance with the method of this invention can have a preselected specific surface area and corresponding average pore diameter within a wide range by manipulating processing conditions. As used herein, the phrases "high surface area" and "high specific surface area" mean a specific surface area at least about 100 m²/g, preferably at least about 150 m²/g. The range of specific surface areas typically achievable when using the method of this invention is from about 200 to about 600 m²/g and the corresponding average pore diameters range from about 50 to about 200 Angstroms.

Silica prepared in accordance with the method of the invention will have a narrow distribution of pore diameters around the selected value. Typically, the standard deviation in pore diameter is less than about 25 percent of pore size, preferably is less than about 15 percent of pore size and most preferably is between about 5 and 10 percent of the size, i.e., at an average pore diameter of 75 Angstroms, the standard deviation is between about 3.75 and 7.5 Angstroms. The conditions under which the silica gel is prepared determine the specific surface area and average pore diameter of the gel product.

Silica gel is the reaction product of water and silicon tetrafluoride, in accordance with the following reaction equation:



The reaction of silicon tetrachloride yields silica and hydrogen chloride, as follows:



Silica gel formed by these exothermic reactions is washed, ground, and classified by particle size. It then can be used as normal phase liquid chromatography column packing or can be modified by reaction with organochlorosilanes to produce reversed phase packing.

Hydrolysis of silicon tetrafluoride in accordance with the invention yields 1 mol of silica for every 3 mols of silicon tetrafluoride. It has been discovered that a minor amount of ammonium hydroxide (up to about 1 wt percent NH₄OH) may be added to the water to increase the rate of gelation and to produce a favorable effect on the acidity of gel made from silicon tetrafluoride.

Hydrolysis of silicon tetrachloride in accordance with the invention is much more efficient than is preparation of gel from silicon tetrafluoride, as 100 percent of the silicon is available to form silica. However, the period required to form a gel by reaction with water is quite long. It has been discovered that addition of fluoride ions to the water used to hydrolyze silicon tetrachloride not only accelerates gelation but also affords a measure of control over the properties of the gel product which cannot be attained by known methods of hydrolyzing silicon tetrachloride. Further, it has been discovered that the specific surface area of gel produced by hydrolysis of silicon tetrachloride which is

aged for about 4 hours after gel formation is affected by the temperature at which the gel is aged.

Silicon tetrafluoride may be obtained from many sources. Typically, silicon tetrafluoride used in the present invention is recovered as a by-product of the wet process acid (WPA) method for obtaining phosphoric acid. However, silicon tetrafluoride from any source is suitable for use in the method of the invention if it is reasonably pure. For purposes of this invention, the silicon tetrafluoride should have substantially no impurities which would adversely affect the purity and quality of the silica product.

Similarly, silicon tetrachloride essentially free of impurities which would adversely affect the purity and quality of the silica product may be used in the method of the invention. Such material may be obtained from diverse sources.

The concentration of silicon tetrahalide in the solvent can range up to the concentration at which silicon tetrahalide is saturated in the solvent. The differences between the saturation concentrations of silicon tetrafluoride and of silicon tetrachloride in solvents used in the method of this invention are not significant for the purposes of the invention. It has been discovered that specific surface area of silica gel is decreased by excessively high silicon tetrahalide concentration in the solvent. Therefore, although silicon tetrahalide concentration in solvent may range beyond 40 wt. percent, preferred silicon tetrahalide concentrations are less than the saturation concentration and in the range about 5 to 40 wt. percent, more preferably between about 8 and 30 wt. percent, and most preferably between about 10 and 20 wt. percent, based on the weight of the solvent.

Suitable solvents are those able to act as solute for silicon tetrahalide without forming silica gel. Further, the solvent is preferably sufficiently soluble with water so that at least a stoichiometric quantity of water will be available for reaction with the silicon tetrahalide absorbed therein. The solvent should also be fluid at room temperature (i.e., less than about 30° C.).

Suitable solvents for silicon tetrahalide include selected alcohols. Both saturated and unsaturated aliphatic alcohols are preferred in the subject invention. Low molecular weight alcohols are especially preferred because the solubility of the alcohol in water increases as the molecular weight decreases. Thus, the C₁-C₃ aliphatic alcohols, including alicyclic alcohols such as cyclopentanol, are preferred, while the C₁-C₄ aliphatic alcohols are most preferred, and the C₁-C₃ aliphatic alcohols are most preferred. The most preferred alcohols are completely miscible with water. Normally, alcohols having an aromatic moiety, such as phenols, are typically insufficiently soluble in water or are not fluid at about 30° C. to be useful as a solvent.

Under certain conditions, alkoxysilicon compounds may form when silicon tetrahalide is added to the solvent. For example, addition of silicon tetrachloride to methanol may result in formation of a volatile component such as hydrogen chloride and produce methoxysilicon-containing compounds in accordance with the reaction



The presence of these compounds does not interfere with the subsequent silica gel formation. The exothermic nature of the dissolution of silicon tetrachloride in methanol requires not only that silicon tetrachloride be

mixed into methanol, but also that the rate at which silicon tetrachloride is added be controlled to prevent overheating of the solution. In contrast, one wishing to produce tetramethoxysilane, i.e., $\text{Si}(\text{OCH}_3)_4$, in a batch process would add the methanol to the silicon tetrachloride.

Solvent should be essentially free of impurities and contaminants which adversely affect the product silica gel. The solution of silicon tetrahalide in solvent also should be essentially free of trace impurities such as metals which, if incorporated into the silica gel structure, affect the surface properties of the silica gel particles. Similarly, the solvent should be free of contaminants which hydrolyze or otherwise react with silicon tetrahalide.

Thus-prepared silicon tetrahalide solution then is rapidly mixed with water, which contains fluoride ion if the halide is chloride, and is agitated to ensure thorough mixing. The water must have essentially no impurities which are proscribed from the solvent, as described above. For example, water which has been de-ionized and filtered, then distilled is suitable for use in this invention. Thus-treated water may have an electrical resistance of about 1 mega-ohm.

After the components are well mixed to ensure intimate contact between the water and the silicon tetrahalide, the resulting gelling medium (i.e., the mixture of water and silicon tetrahalide-containing solution) is allowed to stand without further agitation. The period required for gel formation varies with reaction conditions, and typically is less than about 24 hours. It has been discovered that the specific surface area properties of dried gel product can be further influenced by aging gel produced by hydrolysis of silicon tetrahalide for about four hours, as described below.

The identity of the silicon tetrahalide determines the reactants used, the manner in which the gel is produced, and whether postgellation treatment is required. Preparation of the silicon tetrahalide solution differs significantly. Silicon tetrafluoride is a gas at ambient conditions, and is sparged or bubbled into the solvent until a predetermined concentration is achieved. Because the heat of dissolution of silicon tetrafluoride in solvents described herein is small, the temperature of the solution is essentially the same as the starting temperature of the solvent. Silicon tetrachloride is liquid at ambient temperature, and is therefore easier to handle than gaseous silicon tetrafluoride. However, because the heat of dissolution of silicon tetrachloride in solvent is much larger than that of silicon tetrafluoride, care must be exercised to ensure that the solution doesn't boil. Further, HCl is evolved from the solution. Thus, silicon tetrachloride is added slowly to solvent until the desired concentration is reached. Preferably, the solution temperature does not exceed about 50° C. The solution may be cooled, if necessary.

When silicon tetrafluoride is utilized, the reactants typically are at or below ambient temperature before mixing. Any temperature at which all reactants are liquid is acceptable. Hydrolysis of silicon tetrafluoride is an exothermic reaction. If the gelling medium is not externally cooled during the hydrolysis reaction, the temperature will rise as the reaction proceeds. Preferably, the gelling medium is not allowed to boil.

External cooling can be utilized, but typically is not necessary. Reactant solutions can be cooled conveniently before mixture. Although the temperature increase resulting from the heat of reaction of silicon

tetrafluoride will vary with the quantity of gelling medium in which the heat is absorbed, seldom will the temperature exceed 50° C. in accordance with the practice of this invention. Therefore, cooling generally is not needed to remove the exothermic heat of reaction.

The time required to form the gel depends upon reaction conditions and varies from a few seconds to about 24 hours.

At least a stoichiometric quantity of water preferably is utilized to hydrolyze the silicon tetrafluoride. Utilizing less than a stoichiometric quantity of water, i.e., using less than 2 mols of water per 3 mols of silicon tetrafluoride, precludes recovery of a theoretically expected quantity of silicon as silica, and thus is inefficient.

It also has been discovered that specific surface area of silica product is affected by the quantity of water present. Increasing the quantity of water beyond the stoichiometric minimum increases the specific surface area of the gel. Preferably, a stoichiometric excess of water is used to maintain a water to silicon tetrafluoride mass ratio of at least about 2:1, more preferably between about 2:1 and 20:1, and most preferably between about 4:1 and 10:1. Additional water also serves as a heat sink for the exothermic heat of reaction.

Although use of ammonia as an adjuvant during gelation is not required in the practice of this invention, use of a minor amount of ammonia when hydrolyzing silicon tetrafluoride has been discovered to have a salutary effect on the rate of gelation and the acidity of the gel product. Preferably, the amount of ammonium hydroxide does not exceed about 1.0 wt percent based on the weight of the water, more preferably does not exceed about 0.5 wt percent, and most preferably does not exceed about 0.3 wt percent. It has been discovered that silica gel product obtained with more than about 1 wt. percent ammonium hydroxide in the water is weak and powdery. Thus, such product is not suitable for use in high performance liquid chromatography columns. Lack of strength allows silica gel particles to be crushed under pressure. Due to the powdery nature and poor strength of such silica, fines are generated during loading and use. These fines tend to block the liquid chromatography column, impeding flow and causing pressure to increase while reducing the efficiency of the column.

When silicon tetrachloride is hydrolyzed in accordance with the method of the invention, fluoride ions are present in the water when the water and the silicon tetrachloride-containing solvent are mixed. Fluoride ion may be derived from any source which does not contribute deleterious impurities to the water. Thus, the aqueous solution of fluoride may be obtained by dissolving pure ammonium fluoride crystals in pure water or from hydrofluoric acid solution.

The concentration of fluoride ion in water is up to about 6 wt. percent, and preferably is between about 1 and 6 wt percent. It has been discovered that the ratio of fluoride ion to silicon tetrachloride has a significant effect on the specific surface area and yield of silica product. Typically, yield declines as this ratio is increased, except at low (up to about 1 wt percent) fluoride concentration in water, where the relationship is reversed. Specific surface area typically moves through a minimum as the ratio is increased. Skilled practitioners will be able, with the guidance provided herein, to determine these relationships with specificity.

Hydrolysis of silicon tetrachloride also is an exothermic reaction which is allowed to proceed without cool-

ing at a temperature below the boiling point of the gelling medium. Reactants may be cooled before being combined.

The quantity of water should at least satisfy the stoichiometric requirement, i.e., 2 mols of water per mol of silicon tetrahalide. Preferably, a large stoichiometric excess of water is utilized, i.e., between about 5 and 60 mols of water per mol of silicon tetrachloride, more preferably between about 5 and 30 mols of water per mol of silicon tetrachloride, and most preferably between about 10 and 30 mols of water per mol of silicon tetrachloride.

The time required to complete the reaction depends upon the reaction conditions and can range from a few seconds to hours. In the case of silicon tetrachloride, the reaction rate is increased by increased quantities of fluoride ion. Those skilled in the art will recognize that the conditions which adversely affect specific surface area, as outlined above, such as increasing silicon tetrahalide concentration in the solvent or decreasing the water/silicon tetrahalide ratio, are those conditions which result in a shorter reaction time.

The gel formed by hydrolysis of silicon tetrachloride is aged for about 4 hours at a temperature between the freezing and boiling temperatures, preferably between about 20° and 80° C. It has been discovered that the specific surface area of dried gel thus treated decreases with increasing aging temperature.

The silica gel is separated from the remainder of the reaction mixture by, e.g., suction filtration or centrifugation, then is washed until the pH of the wash water is at least about 3 to remove fluorides, including HF, H_2SiF_6 , and ammonium fluoride, which may be present in the gel. Washing techniques are well known to those skilled in the art. The water used in the wash medium should have the same purity as the water used to hydrolyze the silicon tetrahalide. Typically, the silica gel is soaked in deionized water for about 2 hours, after which the gel is separated by decantation or centrifugation. The pH of the water typically is measured after the gel has soaked in the washing medium for at least about 2 hours. After pH measurement, the washing medium is decanted and fresh wash medium added. The soak/separation cycle is repeated a plurality of times until the pH of the waste wash medium is above about 3, preferably above about 5. It has been discovered that the specific surface area of the silica is increased when the pH of the waste wash medium, and thus of the silica itself, is at least above about 3, and preferably is above about 5, before the gel is further processed. The pH of the gel is determined in 2% aqueous suspension.

The wash medium can be pure water, or can include adjuvants which aid in neutralizing the acidity of the gel. For example, a minor amount of ammonium hydroxide is a useful adjuvant. Generally, the concentration of ammonium hydroxide in the wash medium is less than about 0.010 wt. percent, preferably less than about 0.005 wt. percent.

High specific surface area silica gel thus washed then is dried, ground, and classified according to particle size. Before grinding, the specific surface area and pore size can be determined. Methods for determining these characteristics are well known in the art. For example, specific surface area can be determined by single point or multiple point BET. Similarly, pore size distributions can be determined by capillary condensation and multilayer adsorption/desorption of nitrogen, or an automatic porosimeter.

Silica gel prepared in accordance with the method of this invention is dried in air by a method known in the art. During this time, the temperature typically does not exceed about 200° C., and preferably does not exceed about 150° C. The dried silica gel typically has a moisture content less than about 5 wt. percent, preferably less than about 3 wt. percent, based on the weight of the silica gel.

Characteristics of the silica gel may be determined before or after the gel is ground and classified to yield a predetermined particle size. Typical particle sizes used for liquid chromatography column packing include 5 microns and 10 microns. Preferably, particles less than 2 microns are removed because such small particles cause excessively high pressure drop in packed columns. Any particle size reduction method which does not introduce unacceptable quantities of impurities into the gel particles can be utilized to achieve the selected particle size. Such methods are known to skilled practitioners.

Particles to be used in chromatographic applications, and for other water-sensitive uses, should be further dried to eliminate essentially all water molecules associated with the surface of the gel particle. This additional drying step is carried out by methods known in the art, such as heating gel particles to between about 120° C. and 200° C. in a vacuum of 28 inches of mercury for about 24 hours.

Failure to properly dry the silica gel will result in a gel product which is not suitable for chromatographic separations. Water on the surface of the gel particle affects the form of the silanol group on the particle. The surface of silica gel may comprise individual silanol groups (SiOH), hydrogen bonded (vicinal) silanol groups ($(\text{SiOH})(\text{HOSi})$), and geminal silanol groups ($(\text{SiOH})_2$). The presence of water facilitates changes in form. Although all forms are useful in chromatography, it is more difficult to maintain consistent results when the form of silanol is not consistent. Therefore, careful drying is important.

The method of the invention yields silica gel which is more acidic (determined in 2% aqueous suspension) than most commercially available silica gels. Acidic silica is thought to be more efficient for chromatographically separating neutral and acidic solutes than basic, nitrogen-containing solutes. Acidic gels may cause variable retention times and excessive peak tailing for basic compounds for reasons known to those skilled in the art.

Dilute hydrofluoric acid wash typically is used to condition silica before bonding stationary phases thereto. Such conditioning improves separation efficiency and sample recovery because the surface silanols are fully hydroxylated, i.e., form individual silanol groups. Such a wash is not necessary for gel made in accordance with this invention, however, because individual silanol groups exist when silica is produced in accordance with the method of the invention. The acidity of the gel is believed to be the result of high specific silanol group concentration. Further, the gel is especially suited for use as reverse phase chromatography column packing because organochlorosilanes are bonded preferentially to sites having individual silanol groups.

Organochlorosilane may be bonded as a stationary phase to dried acid-treated silica gel by methods known in the art, such as refluxing organochlorosilane with the silica gel. Catalyst such as pyridine and other organic bases may also be used. The monochloro forms of or-

ganochlorosilanes are preferred because they form a monolayer stationary phase. The monofunctionality of the molecule, which results from the single chlorine moiety, precludes reactions which would form a polymeric, multi-layered stationary phase. To ensure improved separation reproducibility by minimizing undesired interaction between residual silanol and the mobile phase, the stationary phase is endcapped with a constituent which makes the stationary phase essentially unreactive. Chlorotrimethylsilane is a preferred endcap constituent. The silica gel product thus prepared is ready for use as column packing for reverse phase liquid chromatography.

The following examples illustrate various aspects of this invention, but are in no way intended to narrow the scope of the invention. The scope of the invention is limited only by the scope of the appended claims.

EXAMPLES

Unless otherwise identified, reagents and solvents utilized in the following examples were purchased from commercial sources and were used without additional purification:

Silicon tetrafluoride (Matheson, 99.99% min.)
Silicon tetrachloride (Alfa or Aldrich)
Ethanol (Fisher, 100%)
Methanol (Fisher, 99.9%)
Ammonium Hydroxide (Fisher, 28-30%)
Ammonium Fluoride
Hydrogen Fluoride
Deionized water-processed in a Barnstead Nanopure II Cartridge System and distilled (MP-6 Angstrom Megapure System).

EXAMPLE 1

Silica gel was prepared by hydrolysis of silicon tetrafluoride in accordance with the method of the invention to study the effect of varying reactant concentrations on specific surface area. The data are summarized in Table 1.

Silicon tetrafluoride was bubbled into anhydrous ethanol until a preselected concentration was achieved. In an ice water bath, a predetermined quantity of water was rapidly mixed with the silicon tetrafluoride/ethanol solution with brief agitation and then allowed to stand. The temperature of the mixture increased between about 5 and 25° C., depending upon reaction conditions. The time required for gel formation, also dependent upon reaction conditions, varied from seconds to hours.

The concentration of silicon tetrafluoride in ethanol was 16 wt. percent in all samples. The specific surface area was determined by single-point BET, using a Quantasorb QS10 device. The samples were outgassed for 4 hours under helium atmosphere at 200° C.

TABLE 1

Sample No.	Gel Preparation		SSA (m ² /g)
	H ₂ O/SiF ₄ Mass Ratio	NH ₄ OH (%)	
1A	4:1	0.0	326
1B	6:1	0.0	331
1C	8:1	0.0	366
1D	4:1	0.1	331*
1E	6:1	0.1	346
1F	8:1	0.1	383
1G	4:1	1.0	231
1H	6:1	1.0	294
1I	8:1	1.0	315
1J	4:1	5.0	57
1K	6:1	5.0	144
1L	8:1	5.0	198

*Average of 3 tests.

This example shows that the specific surface area increases with increased water/silicon tetrafluoride mass ratio, and is maximized when up to about 1 wt. percent ammonium hydroxide is present.

EXAMPLE 2

Silica gels were prepared by hydrolyzing silicon tetrafluoride in accordance with the method of this invention under the following conditions:

Reaction temperature=10°-25° C. in an ice bath.

Water/silicon tetrafluoride, weight ratio=8

Ammonium concentration in water=0.1 wt. percent

Silicon tetrafluoride/ethanol=16 wt. percent

Each of the preparations was air dried. Because specific surface area is a difficult determination, both six point and single point BET were obtained. Single point BET's were processed as described in Example 1. For the multiple point BET's, samples were outgassed to 0.02 Torr vacuum at 200° C. The data are summarized in Table 2.

TABLE 2

Sample No.	Results of HPLC Gel Preparation					BET Specific Surface Area (m ² /g)	
	SiF ₄ (g)	EtOH (g)	SiF ₄ Conc. (%)	Prod. Gel (g)	Yield (%)	Six-point	Single Point
2A	785	4127	16.0	91.1	60.3	521	490
2B	787	4135	16.0	99.3	65.6	444	646
2C	810	4263	16.0	99.0	63.6	573	680
2D	769	4019	16.1	90.0	60.9	487	511
2E	810	4243	16.0	99.2	63.7	550	554
2F	813	4266	16.0	96.8	61.9	540	444

Table 3 summarizes specific surface area and pore diameter information for the samples described in Table 2. Pore diameter was calculated in three ways known to those skilled in the art. The low standard deviation for each determination illustrates the consistency of result achieved when practicing the method of the invention.

TABLE 3

	Summary of Pore Size Analysis						Standard Deviation
	Sample No.						
	2A	2B	2C	2D	2E	2F	
Total Pore Volume (cc/gm)	0.87	0.87	0.92	0.93	0.79	0.84	0.052
Total Surface Area (m ² /gm)	520.82	554.75	572.89	487.22	550.32	540.15	
Avg. pore Dia. (A) (Calculated from 4 V/S BET)	66.55	62.85	64.41	76.43	57.20	62.09	6.44
Median Pore Dia. (A)	80.09	74.57	74.27	96.72	67.96	77.05	9.81

TABLE 3-continued

Summary of Pore Size Analysis							
	Sample No.						Standard Deviation
	2A	2B	2C	2D	2E	2F	
(Based on pore vol.)							
Median Pore Dia. (A)	53.39	49.78	51.67	63.55	45.93	50.61	5.96
(Based on surface area)							
Avg. Pore (Dia. (A) - 3 Methods	66.88	62.40	63.45	78.90	57.03	63.25	

EXAMPLE 3

Samples 2A and 2B, prepared as described in Example 2, were combined, ground, and classified into preselected size ranges. About one-half (96 g) of the material was recovered in five products, as described below.

Product 3A: milled straight to 5 microns and not classified (23 g)

Products 3B1 and 3B2: milled to 10 microns, classified, coarse portion (23 g and 37 g)

Products 3C1 and 3C2: milled to 10 microns, classified, fine portion (3 g and 10 g)

Table 4 below summarizes the particle size distribution for these products and for Amicon's Matrex® 10 micron, 100 Angstrom product after removal of the sub-micron particles. The data indicate that the products of the invention have particle size distributions which are appropriate for use in HPLC.

TABLE 4

Percent Smaller Than	Amicon ¹	Product				
		3A	3B1	3B2	3C1	3C2
2 microns	1	13	2	2	13	13
4 microns	8	42	13	13	47	42
6 microns	18	70	24	24	72	70
8 microns	23	89	35	37	90	88
10 microns	36	94	48	52	95	94
15 microns	61	99	68	73	99	99
20 microns	82	100	86	89	100	100

¹Matrex® 10 micron; 100 Angstrom pores

Sample 3B2 was bonded with chlorodimethyloctadecylsilane and endcapped with chlorotrimethylsilane in accordance with the above-described method of preparing reversed phase silica gels. The sample, labeled 3B2-Bond, had particle size of 10 microns and pore diameter of 64 Angstroms.

The pH and chemical analysis of various products of this invention and commercially available products are illustrated in Table 5 below. The relatively low impurity levels, especially aluminum, iron, and water-extractable fluorine and silicon, in Sample 3B2-Bond of the invention are attributed to the conditioning prior to bonding and solvent washing thereafter.

Table 5 illustrates that products of the invention typically have lower metal ion concentrations than do other commercially available products. The iron and aluminum levels in products 3A and 3C2 of the invention are higher than these iron levels of unprocessed Product Si. The higher iron content is due to the use of the hammer mill during size reduction, and slightly higher aluminum contents are due to the classifier. Products of the invention have a relatively low pH and high water extractable fluorine content, which can be removed by conditioning, as described in the specification.

TABLE 5

Comparison of Impurities Present in Various Silica Products								
Sample	Product Si ^a	Product 3A	Product 3C2	3B2- Bond	Amicon	Whatman	Zorbax ^b	LiChropur ^b
Surface pH (2% suspension in water)								
	2.92	2.99	2.88	4.48	6.42	4.58	4.3	—
Chemical Analysis (ppm)								
Na	1.3	8.5	11.9	15.5	439	8.5	105	2900
K	0.6	1.7	2.4	<5	41	2.1	—	—
Li	<0.2	<1	<1	<1	<0.2	<0.2	<5	<5
Ca	2.8	0.1	5.6	17.5	493	168	<5	<5
Mg	1.3	6.3	9.1	4.3	112	41	—	—
Al	1.2	20.0	23.4	2.3	146	51	1100	—
Fe	2.3	44.6	69.6	7.5	46	28	445	68
Co	0.0	0.7	0.9	0.0	0.1	0.0	—	—
Ni	0.1	1.3	2.1	0.5	0.0	0.1	—	—
Cu	0.1	7.6	9.2	0.4	0.2	0.2	245	—
Mn	0.1	0.8	1.0	0.6	0.5	0.4	—	31
Pb	0.6	2.0	4.2	0.0	1.8	0.7	—	—
Ba	0.2	16.8	41.0	0.6	18.8	4.1	—	81
Cd	0.0	0.2	0.2	0.0	0.0	0.0	—	—
Cr	0.1	1.7	2.0	2.0	1.5	0.4	115	—
Mo	0.0	0.1	0.3	0.0	0.0	0.0	—	—
Sr	0.0	0.1	0.2	0.0	1.8	0.5	—	—
Zn	0.4	6.4	19.8	0.6	0.8	0.5	—	—
P	0.8	4.6	5.4	0.0	0.4	0.2	—	—
S	12.4	2.9	11.7	0.0	70.5	13.8	—	—
V	0.0	0.4	0.5	0.7	0.3	0.0	—	—
F % ^c	0.52	0.31	0.50	0.01	—	—	—	—
Si % ^c	—	0.29	0.34	0.21	—	—	—	—
Cl	—	—	—	—	—	—	—	—

TABLE 5-continued

Comparison of Impurities Present in Various Silica Products								
Sample	Product Si ^a	Product 3A	Product 3C2	3B2- Bond	Amicon	Whatman	Zorbax ^b	LiChropher ^b
SO ₂					300			

^a100-gram batch of silica from the combination of Samples 2A and 2B before grinding and sizing.

^bNot derived from chemical analysis.

^cWater extractable.

EXAMPLE 4

The separation performance of silica columns of the invention (silicon tetrafluoride hydrolysis) was compared with column packed with Amicon Matrex® silica. The liquid chromatograph system consisted of a Waters 590 solvent delivery pump, a Beckman 210 sample injection valve, a Waters 481 variable UV-VIS detector, and a Waters 740 recorder. Flowrates of 0.5, 1.0, and 2.0 ml. per minute were used for constructing the van Deemeter plots. The following four sets of compounds were injected in this column evaluation:

I. Toluene, 1,3-dinitrobenzene, benzaldehyde
II. Toluene, nitrobenzene, acetophenone, 2,6-dinitrotoluene

III. Dimethyl-, diethyl-, and dibutylphthalate homologues

IV. 1,2-, 1,3-, and 1,4-dinitrobenzene isomers

Toluene was used as the void volume marker in normal phase chromatography. The mobile phase solvents for each set were:

I. hexane:methylene chloride 44:56 (v/v)

II. hexane:ethyl acetate 98:2 (v/v)

III. isooctane:tetrahydrofuran 95:5 (v/v)

IV. isooctane:tetrahydrofuran 95:5 (v/v)

Overall separation performance was based on the resolution equation:

$$R_s = \frac{N^{\frac{1}{2}}}{4} \left(\frac{\alpha - 1}{\alpha} \right) \left(\frac{k'}{1 + k'} \right) \quad (4)$$

$$k' = \frac{t - t_0}{t_0} \quad (5)$$

where

R_s : overall resolution between two adjacent peaks

N : column plate count

k' : solute capacity factor

α : selectivity ($=k'_2/k'_1$)

t_0 : column void time (seconds)

The first term is indicative of column efficiency (i.e., peak sharpness), the second term selectivity (i.e., distance between two peaks), and the third term retention capacity or loading.

The separation of compound Set I is illustrated in FIG. 1 for four different columns. The corresponding van Deemeter plots are shown in FIG. 2 and the overall performance (i.e., R_s), including efficiency, selectivity,

and capacity, is shown in Table 6. Because of the higher surface area which provides greater retention capacity, the silicas of the invention had several advantages over the Amicon silica:

1) About 10% better overall separation performance for 10 micron silica (i.e. 3B2). The 30% better capacity was achieved at the expense of column efficiency (about 15% less) due to longer retention time. This can be seen in FIG. 2 where 3B2 has slightly larger HETP values (i.e. lower N plate counts) than Amicon.

2) For 5 micron Products 3C2 and 3A-Dried columns, about 100% better overall performance was realized because of not only higher efficiency due to smaller particle size but also higher retention capacity. Small-size particles tend to yield less dispersion in both interstice void zones and micropores. The relatively large portion (about 13 percent) of particles sized up to 2 microns in these samples necessitated the high pressure drop for these columns. Amicon does not have 5 micron silica products.

The loading capacity of silica columns made in accordance with the invention was compared to that of the Amicon product. The overall performance decreased with increasing sample size (Table 7) when the sample concentration remained constant. A sample loop one order of magnitude greater (from 20 to 200 microliter) in the 3C2 column yielded better resolution than Amicon column (20 microliter loop), demonstrating that silica of the invention can be used for large-scale operations. A side-by-side comparison of columns overloaded with a mixture (FIG. 3) further indicates that both Product 3B2 and 3C2 silica columns can achieve baseline separation for a desired component in mixtures, thus improving product purity and throughput.

Silica columns prepared in accordance with the invention also performed better than the 10-micron Amicon column for separations of aromatic compounds (Set II, FIG. 4), homologues (Set III, FIG. 5), and isomers (Set IV, FIG. 6) under identical conditions. The overall separation performance on Sets II and III is summarized in Tables 8 and 9. A plate count of greater than 60,000/meter was achieved for Product 3A column at a flowrate of 1.0 ml/min for the separation of Set II samples. This high plate count, achieved by irregular silica, is comparable to plate counts achieved by spherical silica.

TABLE 6

Overall Separation Performance for Products of the Invention and Amicon Columns Separation Set I: Toluene, 1,3-Dinitrobenzene, Benzaldehyde ¹						
Column (Part. Size + Deviation) ²	Flowrate (ml/min)	Pressure Drop (psi)	Efficiency $\sqrt{N}/4$	Selectivity ($\alpha-1$)/ α	Capacity $k'/(1+k')$	Overall R_s
Amicon	2.0	110	11.8	0.52	0.53	3.3
(13.2	1.0	6	13.2	0.53	0.54	3.8
7.6 microns)	0.5	0	13.9	0.54	0.54	4.1
IMC 3B2	2.0	232	10.5	0.53	0.70	3.9

TABLE 6-continued

Overall Separation Performance for Products of the Invention and Amicon Columns Separation Set I: Toluene, 1,3-Dinitrobenzene, Benzaldehyde ¹						
Column (Part. Size + Deviation) ²	Flowrate (ml/min)	Pressure Drop (psi)	Efficiency $\sqrt{N}/4$	Selectivity (α -1)/ α	Capacity $k'/(1+k')$	Overall R_s
(10.9 6.8 microns)	1.0	34	11.1	0.53	0.71	4.2
	0.5	0	12.1	0.53	0.71	4.6
Product 3C2	2.0	2380	17.8	0.51	0.71	6.4
(4.9 2.6 microns)	1.0	1080	20.0	0.51	0.71	7.2
	0.5	450	20.5	0.51	0.72	7.5
Product 3A-Dried	2.0	2950	22.4	0.50	0.70	7.8
(4.9 2.5 microns)	1.0	1300	24.5	0.50	0.71	8.7
	0.5	580	23.5	0.51	0.72	8.6
Product 3A-Not Dried	2.0	2580	5.2	0.51	0.69	1.8
(4.9 2.5 microns)	1.0	1170	5.1	0.51	0.70	1.8
	0.5	513	6.4	0.50	0.71	2.3

¹N and k' were determined using the dinitrobenzene peak, α using dinitrobenzene and benzaldehyde peaks.²Deviation was measured using the sizes at 84% and 16% cuts.

TABLE 7

Overall Separation Performance for Overloaded Columns Separation Set I: Toluene, 1,3-Dinitrobenzene, Benzaldehyde ¹					
Column	Sample Loop (microliter)	Efficiency $\sqrt{N}/4$	Selectivity (α -1)/ α	Capacity $k'/(1+k')$	Overall R_s
Amicon	20	13.2	0.53	0.54	3.8
	100	12.8	0.51	0.48	3.1
	200	11.3	0.46	0.44	2.3
	500	8.6 ²	0.52	0.51	2.3
Product 3B2	20	11.1	0.53	0.71	4.2
	100	11.2	0.49	0.66	3.6
	200	10.4	0.48	0.61	3.0
	500	9.3 ²	0.51	0.65	3.1
Product 3C2	20	20.0	0.51	0.71	7.2
	100	19.0	0.49	0.70	6.5
	200	17.7	0.49	0.71	6.2
	500	15.0 ²	0.49	0.66	4.8

¹Sample concentration: toluene 0.04 mg, 1,3-dinitrobenzene 0.001 mg, benzaldehyde 0.006 mg in 10 ml mobile phase solvent (hexane:methylene chloride 44:56 by volume)²Bandwidth is estimate due to off-scale peak.³ $R_s = 1.5$ for baseline resolution (Equation 4).

TABLE 8

Overall Separation Performance Separation Set II: Toluene, Nitrobenzene, Acetophenone, 2,6-Dinitrotoluene ¹					
Column (Part. Size + Deviation) ³	Flowrate (ml/min)	Efficiency $\sqrt{N}/4$	Selectivity (α -1)/ α	Capacity $k'/(1+k')$	Overall R_s
Amicon	2.0	12.0	0.65	0.52	4.2
(13.2 7.6 microns)	1.0	12.6	0.67	0.53	4.5
	0.5 ²	15.1	0.65	0.52	5.1
Product 3B2	2.0	11.8	0.64	0.63	4.8
(10.9 6.8 microns)	1.0	11.5	0.65	0.60	4.5
	0.5 ²	14.3	0.66	0.63	5.9
Product 3C2	2.0	18.8	0.64	0.61	7.3
(4.9 2.6 microns)	1.0 ²	20.4	0.64	0.61	8.0
	0.5	19.7	0.64	0.61	7.7
Product 3A-Dried	2.0	24.4	0.64	0.62	9.7
(4.9 2.5 microns)	1.0 ²	30.8	0.64	0.62	12.2
	0.5	23.4	0.69	0.66	10.7

¹N and k' were determined using the acetophenone peak, α using acetophenone and dinitrotoluene peaks.²Optimal flow rate 0.5 ml/min. for Amicon and Product 3C columns, 1.0 ml/min. for Products 3B and 3A-Dried columns ($n = 15200$).³Deviation was measured using the sizes at 84 & 16% cuts.

TABLE 9

Overall Separation Performance Separation Set III: Dibutyl-, Diethyl-, Dimethyl-Phthalate Homologues ¹					
Column (Part. Size + Deviation)	Flowrate (ml/min)	Efficiency $\sqrt{N}/4$	Selectivity (α -1)/ α	Capacity $k'/(1+k')$	Overall R_s
Amicon	2.0	11.1	0.59	0.47	3.1

TABLE 9-continued

Overall Separation Performance Separation Set III: Dibutyl-, Diethyl-, Dimethyl-Phthalate Homologues ¹					
Column (Part. Size + Deviation)	Flowrate (ml/min)	Efficiency $\sqrt{N}/4$	Selectivity ($\alpha-1$)/ α	Capacity $k'/(1+k')$	Overall R_s
(13.2 7.6 microns)	1.0 0.5	12.4 12.2	0.60 0.61	0.47 0.48	3.5 3.6
Product 3B2 (10.9 6.8 microns)	2.0 1.0	9.3 10.5	0.55 0.54	0.55 0.55	2.8 3.1
Product 3C2 (4.9 2.6 microns)	2.0 1.0	16.7 20.0	0.55 0.55	0.56 0.56	3.4 5.1
Product 3A-Dried (4.9 2.5 microns)	0.5 2.0	21.1 20.0	0.55 0.56	0.56 0.60	6.2 6.5
	1.0	20.8	0.55	0.59	6.7
	0.5	28.4	0.53	0.59	8.9

¹N and k' were determined using the dimethylphthalate peak, α using diethyl- and dibutyl-phthalate peaks.
²Deviation was measured using the size at 84 and 16 percent

EXAMPLE 5

Silica gel was produced in accordance with the method of this invention, wherein the concentration of silicon tetrafluoride in methanol solvent was varied to determine the effect of this parameter on specific surface area.

Silicon tetrafluoride was bubbled through alcohol until the desired concentration was reached. A quantity of 0.1 wt. percent ammonium hydroxide sufficient to make the wt. ratio of ammonia solution to silicon tetrafluoride equal 8 then was added to the alcohol solution. The mixture was briefly agitated to ensure proper mixing, then was allowed to set. The heat of reaction raised the temperature of the mixture from room temperature to about 38° C.

After 24 hours, the gel was collected by suction filtration or centrifugation, then was washed with deionized water containing 0.003 percent NH_4OH , followed by deionized water, until the pH of the wash water was greater than 5.0. The gel was allowed to soak for at least 2 hours before the pH was determined. After a pH of at least 5 was obtained, the gel was collected by suction filtration and dried at 150° C. for 15 hours at a vacuum of about -28 to -29 inches Hg. The data summarized in Table 10 illustrate that specific surface area decreases as silicon tetrafluoride concentration increases.

TABLE 10

Sample	Silicon Tetrafluoride Concentration Wt. Percent	Specific Surface Area, m^2/g
A	13	570
B	16	535
C	20	490
D	24	440
E	26	405
F	31	390

EXAMPLES 6A-D

Silica gel products having selected specific surface areas and average pore diameters were prepared in accordance with the method of this invention as described in Example 5. Process parameters were varied to achieve the preselected product characteristics.

Silicon tetrafluoride was bubbled through alcohol to achieve a preselected silicon tetrafluoride concentration. A predetermined amount of 0.1 wt. percent ammonium hydroxide then was added to the alcohol solution and the mixture was briefly agitated to ensure proper mixing. The gelling medium then was allowed to stand

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without further agitation. Each reaction was started at a temperature of 22° C., and none exceeded 38° C. as the heat of reaction evolved.

After 24 hours, the gel was collected by suction filtration or centrifugation and washed until the pH of the waste water wash was greater than 5.0 with deionized water having an ammonium hydroxide concentration of 0.003 percent, followed by pure deionized water. During the washing cycle, the gel was allowed to soak in the wash for approximately 2 hours before the pH was tested. Spent wash medium then was decanted and fresh wash was added. Upon obtaining a pH of at least about 5 in the waste wash medium, the gel was collected via suction filtration and dried at 150° C. for 15 hours under vacuum.

The following tables illustrate the results of these preparations.

TABLE 11A

Desired Specific Surface Area		550 \pm 30 m ² /g	
Average Pore Diameter		60 Angstroms	
Pore Volume		0.88 cc/g	
Sample	Solvent	% SiF ₄ in Solvent	Actual Specific Surface Area, m ² /g
6A-1	Ethanol	16	585
6A-2	Ethanol	16	551
Avg. of 6 Runs ¹	Ethanol	16	538

Note:

¹These runs started at a temperature of 10° C.²Mass ratio of 0.1 wt. percent ammonium hydroxide solution to SiF_4 is 8.

TABLE 11B

Desired Specific Surface Area		460 \pm 30 m ² /g	
Average Pore Diameter		86 Angstroms	
Pore Volume		1.01 cc/g	
Sample	Solvent	% SiF ₄ in Solvent	Actual Specific Surface Area, m ² /g
6B1	Methanol	16	468
6B2	Methanol	16	443
6B3	Ethanol	16	522
6B4	Ethanol	16	487
6B5	Methanol	16	452
6B6	Methanol	16	477
6B7	Methanol	16	430
6B8	Methanol	16	460
6B9	Methanol	16	434

Note: Mass ratio of 0.1 wt. percent ammonium hydroxide solution to SiF_4 is 4.

TABLE 11C

Desired Specific Surface Area		400 \pm 30 m ² /g	
Average Pore Diameter		115 Angstroms	
Pore Volume		1.03 cc/g	
Sample	Solvent	% SiF ₄ in Solvent	Actual Specific Surface Area, m ² /g
6C1	Methanol	32	361
6C2	Methanol	32	423
6C3	Ethanol	32	382
6C4	Ethanol	32	427

Note: Mass ratio of 0.1 wt. percent ammonium hydroxide solution to SiF₄ is 1.

TABLE 11D

Desired Specific Surface Area		230 m ² /g	
Average Pore Diameter		170 Angstroms	
Pore Volume		0.80 cc/g	
Sample	Solvent	% SiF ₄ in Solvent	Actual Specific Surface Area, m ² /g
6D1	Methanol	16	236
6D2	Methanol	16	232

Note: Mass ratio of 0.1 wt. percent ammonium hydroxide solution to SiF₄ is 1.

then separated from the mixture, washed, and dried. Samples were outgassed at 250° C. for about 1-2 hours under helium atmosphere before testing.

The results are illustrated in Table 12.

TABLE 12

Sample	Mols 4% HF Sol'n Mol SiCl ₄	BET Specific Surface Area, m ² /g		Pore Size, Angstroms ¹
		Single Point	Five Point	
7-1	5.1	595	569	57
7-2	5.1	588	591	51
7-3	12.8	333	357	106
7-4	12.8	341	351	107

¹ Twenty-five point analyses on ASAP-2400.

EXAMPLE 8

The normal and reversed phase separation performance of silica columns of the invention (silicon tetrachloride hydrolysis) was compared with Amicon silicas in a liquid chromatograph system as described in Example 4. The properties of the silicas are presented in Table 13.

TABLE 13

Sample	Surface Area (m ² /g) (1)	Pore Vol. (cc/g) (2)	Avg. Pore Size (2)	Avg. Particle Size (3)	Bonding Reagent (4)	Surface Cov. (5)
8-1	550	0.90	66	9.3 \pm 6.2	NA	NA
8-1R	139	0.16	46	11.0 \pm 8.3	TODS	2.71
8-2	319	0.89	112	10.0 \pm 6.7	NA	NA
8-2R	154	0.42	102	13.4 \pm 9.2	TODS	3.14
8-3	320	1.06	132	4.5 \pm 2.4	NA	NA
8-4R	144	0.42	116	5.5 \pm 2.6	MODS	3.11
8-5R	175	0.48	109	4.0 \pm 2.5	TODS	3.90
Amicon 60A	442	0.74	67	9.9 \pm 5.9	NA	NA
Amicon 100A	351	1.26	138	10.2 \pm 6.0	NA	NA
AMIC-C18 (6)	179	0.86	120	10.8 \pm 6.9	TODS	3.34

(1) Surface areas for reversed phase material were measured after endcapping.

(2) Assuming cylindrical pores, Av. Pore Size (Angstroms) = $\frac{40,000 V}{S.A.}$

where V = pore volume and S.A. = surface area.

(3) Microns

(4) NA = Not applicable

TODS = octadecyltrimethylsilane

MODS = chlorodimethyloctadecylsilane

(5) Micromoles/m²

(6) Fractionated to form a 60 Angstrom product (AMIC C18 60A) and a 100 Angstrom product (AMIC C18 100A)

EXAMPLE 7

Silica gel products having selected specific surface area and average pore diameter were prepared in accordance with the method of the invention. Process parameters were varied to achieve the selected product characteristics.

Silicon tetrachloride was dissolved in methanol to obtain a solution containing about 16 wt. percent silicon tetrachloride. A predetermined quantity of 4% HF solution then was added to the alcohol solution, and the mixture was briefly agitated to ensure thorough mixing. The gel which formed was aged at 77° C. for 4 hours,

Two sets of compounds were injected:

8-I. Toluene, 2,6-dinitrotoluene, benzaldehyde

8-II. Uracil, benzaldehyde, benzene, toluene

The mobile phases were:

8-I. Hexane:methylene chloride 44:56(v/v)

8-II. Methanol:water 80:20 (v/v)

Performance was analyzed as described in Example 4. The separation of Compound Set I is illustrated in FIG. 7, and the overall performance is summarized in Table 14. As illustrated therein, the resolution of the product of the invention is comparable to the corresponding Amicon product.

TABLE 14

OVERALL SEPARATION PERFORMANCE FOR PRODUCTS OF THE INVENTION AND AMICON COLUMNS

Separation Set 8-I:

Toluene, 2,6-Dinitrotoluene, Benzaldehyde (I)

Sample	Flowrate (ml/min)	Press. Drop (psi)	Efficiency $\sqrt{N}/4$	Selectivity (alpha-1)/alpha	Capacity k'/(1+k')	Overall R _f
8-1	2.0	760	18.4	0.59	0.62	6.7
	1.0	370	22.1	0.59	0.63	8.2

TABLE 14-continued

OVERALL SEPARATION PERFORMANCE FOR PRODUCTS OF THE INVENTION AND AMICON COLUMNS						
Separation Set 8-I: Toluene, 2,6-Dinitrotoluene, Benzaldehyde (1)						
Sample	Flowrate (ml/min)	Press. Drop (psi)	Efficiency $\sqrt{N}/4$	Selectivity ($\alpha-1$)/ α	Capacity $k'/(1+k')$	Overall R_s
8-2	0.5	200	23.7	0.60	0.62	8.7
	2.0	300	17.2	0.62	0.39	4.2
	1.0	110	19.7	0.64	0.44	5.6
	0.5	10	20.6	0.64	0.45	5.8
Amicon 60A	2.0	314	17.7	0.65	0.60	6.9
	1.0	109	21.3	0.65	0.61	8.3
	0.5	6	23.7	0.65	0.61	9.3
Amicon 100A	2.0	280	19.1	0.69	0.38	5.0
	1.0	95	21.9	0.69	0.38	5.8
	0.5	6	22.8	0.69	0.39	6.1

(1) N and k' were determined using the dinitrotoluene peak, alpha using dinitrotoluene and benzaldehyde peaks.

Reversed phase separation of compound Set II is illustrated in FIG. 8 for four columns. The overall performance of these and other columns is summarized in Table 15. These data illustrate the following:

- (1) Products of the invention having an average pore diameter of 60 Angstroms exhibit better overall performance but less efficiency than Amicon product.
- (2) Amicon's 60A product had better overall resolution, while the overall resolution of the 100 Angstrom products was comparable.
- (3) Higher surface coverage by the bonding reagent improves overall performance, as illustrated by the superior overall performance of sample 8-5R over 8-4R. Octadecyltrichlorosilane provides higher surface coverage than chlorodimethyloctadecylsilane.

1. A method for production of a porous, high specific surface area silica gel having a narrow pore diameter distribution comprising:

- (a) mixing a solution of silicon tetrafluoride and a water-soluble, non-aqueous solvent with at least a stoichiometric quantity of water to form a reactant mixture and to hydrolyze the silicon tetrafluoride to silica;
- (b) permitting the silica to gel;
- (c) separately recovering the silica gel from the remainder of the reactant mixture; and
- (d) washing said silica gel with a washing medium comprising water until the pH of the gel is at least above about 3.

2. The method of claim 1 wherein the concentration of the silicon tetrafluoride solution is between about 5 and 40 wt percent.

TABLE 15

OVERALL SEPARATION PERFORMANCE FOR PRODUCTS OF THE INVENTION AND AMICON COLUMNS						
Separation Set 8-II: Uracil, Benzaldehyde, Benzene, Toluene (1)						
Sample	Flowrate (ml/min)	Press. Drop (psi)	Efficiency $\sqrt{N}/4$	Selectivity ($\alpha-1$)/ α	Capacity $k'/(1+k')$	Overall R_s
8-1R	2.0	2915	9.2	0.60	0.62	3.4
	1.0	1423	9.7	0.60	0.62	3.6
	0.5	663	13.2	0.59	0.61	4.7
8-2R	2.0	2011	12.1	0.56	0.53	3.6
	1.0	1069	13.5	0.56	0.52	3.9
	0.5	520	16.8	0.56	0.52	4.9
AMIC C18 60A	2.0	964	14.3	0.48	0.37	2.5
	1.0	463	18.9	0.47	0.37	3.3
	0.5	198	22.6	0.47	0.37	3.9
AMIC C18 100A	2.0	992	16.0	0.52	0.40	3.4
	1.0	472	20.0	0.53	0.41	4.3
	0.5	200	16.7	0.53	0.41	3.6
8-5k	2.0	NA	NA	NA	NA	NA
	1.0	3250	24.7	0.52	0.48	6.1
	0.5	1570	23.8	0.53	0.48	6.0
8-4R	2.0	4700	20.8	0.50	0.38	3.9
	1.0	2400	24.3	0.50	0.38	4.6
	0.5	1130	26.6	0.50	0.38	4.1

(1) N and k' are determined using the benzaldehyde peak, alpha using benzaldehyde and benzene peaks.

Although preferred embodiments of this invention have been discussed herein, those skilled in the art will appreciate that changes and modifications may be made without departing from the spirit of the invention, as defined in and limited only by the scope of the appended claims.

We claim:

3. The method of claim 1 wherein the solvent is a C₁-C₅ aliphatic alcohol.

4. The method of claim 3 wherein the alcohol is a C₁-C₃ aliphatic alcohol.

5. The method of claim 1 wherein the mass ratio of water to silicon tetrafluoride is at least about 2:1.

6. The method of claim 5 wherein the mass ratio of water to silicon tetrafluoride is between about 4:1 and 10:1.

7. The method of claim 1 further comprising adding to the water of step (a) a quantity of ammonia sufficient to produce in the water an ammonium hydroxide concentration of less than about 1.0 wt percent.

8. The method of claim 1 wherein the washing medium is water having up to about 0.010 wt percent ammonium hydroxide.

9. A method for production of a porous, high specific surface area silica gel having a narrow pore diameter distribution comprising:

(a) mixing a solution of silicon tetrafluoride and a solvent selected from the group consisting of C₁-C₃ aliphatic alcohols with a quantity of water sufficient to form a reactant mixture having a mass ratio of water to silicon tetrafluoride of between about 4:1 and 10:1 and to hydrolyze the silicon tetrafluoride to silica;

(b) permitting the silica to gel;

(c) separately recovering the silica gel from the remainder of the reactant mixture; and

(d) washing said silica gel in a washing medium comprising water until the pH of the gel is at least above about 3.

10. A method for producing silica gel suitable for use in high pressure liquid chromatography comprising:

(a) mixing a solution of silicon tetrafluoride and a solvent selected from the group consisting of C₁-C₃ aliphatic alcohols with a quantity of water sufficient to form a reactant mixture having a mass ratio of water to silicon tetrafluoride of between about 4:1 and 10:1 and to hydrolyze the silicon tetrafluoride to silica;

(b) permitting the silica to gel;

(c) separately recovering the silica gel from the remainder of the reactant mixture;

(d) washing said silica gel in a washing medium comprising water until the pH of the gel is at least above about 3; and

(e) drying said washed gel to obtain dry gel having essentially one form of silanol moiety.

11. A method for production of a porous, high specific surface area silica gel having a narrow pore diameter distribution comprising:

(a) mixing a solution of silicon tetrachloride and a water-soluble, non-aqueous solvent with at least a stoichiometric quantity of water containing fluoride ion to form a reactant mixture and to hydrolyze the silicon tetrachloride to silica;

(b) permitting the silica to gel;

(c) aging the gel for about 4 hours;

(d) separately recovering the silica gel from the remainder of the reactant mixture; and

(e) washing said silica gel with a washing medium comprising water until the pH of the gel is at least above about 3.

12. The method of claim 11 wherein the concentration of the silicon tetrachloride solution is between about 5 and 40 wt percent.

13. The method of claim 11 wherein the solvent is C₁-C₃ aliphatic alcohol.

14. The method of claim 13 wherein the alcohol is a C₁-C₃ aliphatic alcohol.

15. The method of claim 11 wherein the molar ratio of water to silicon tetrachloride is at least about 5:1.

16. The method of claim 15 wherein the molar ratio of water to silicon tetrachloride is between about 5:1 and 30:1.

17. The method of claim 11 wherein the fluoride ion concentration of step (a) is between about 1 and 6 wt percent.

18. The method of claim 11 wherein the washing medium is water having up to about 0.010 wt percent ammonium hydroxide.

19. A method for production of a porous, high specific surface area silica gel having a narrow pore diameter distribution comprising:

(a) mixing a solution of silicon tetrachloride and a solvent selected from the group consisting of C₁-C₃ aliphatic alcohols with a quantity of water containing up to 6 wt percent fluoride ion, said quantity of fluoride ion-containing water sufficient to form a reactant mixture having molar ratio of water to silicon tetrachloride of between about 5:1 and 30:1 and to hydrolyze the silicon tetrachloride to silica;

(b) permitting the silica to gel;

(c) aging the gel for about 4 hours at a temperature between about 20° and 80° C.;

(d) separately recovering the silica gel from the remainder of the reactant mixture; and

(e) washing said silica gel with a washing medium comprising water until the pH of the gel is at least above about 3.

20. A method for producing silica gel suitable for use in high pressure liquid chromatography comprising:

(a) mixing a solution of silicon tetrachloride and a water-soluble, non-aqueous solvent with at least a stoichiometric quantity of water containing fluoride ion to form a reactant mixture and to hydrolyze the silicon tetrachloride to silica;

(b) permitting the silica to gel;

(c) aging the gel for about 4 hours;

(d) separately recovering the silica gel from the remainder of the reactant mixture;

(e) washing said silica gel with a washing medium comprising water until the pH of the gel is at least above about 3; and

(f) drying said washed gel to obtain dry gel having essentially one form of silanol moiety.

• • • • •

APPENDIX D

References Regarding Disclosure in Rostoker Patent

1. U.S. Patent 5,128,081 to Siegel et al.
2. Article by Siegel et al., J. de Physique C5: Supplement
10 681-686 (October 1988).
3. Article by Quintin Ford of Nanophase Corp.
4. Pages from the Nanophase Web Site.

Manufacturing Nanocrystalline Materials by Physical Vapor Synthesis

By Quinton Ford, Director of Marketing, Industrial Products,
Nanophase Technologies Corp., Burr Ridge, Ill.

A CONTINUOUS PROCESS BASED ON GAS-PHASE CONDENSATION CAN PRODUCE NANOCRYSTALLINE PARTICLES IN ECONOMICAL QUANTITIES.

During the past decade, a great deal of research and development has been focused on fabricating and characterizing nanocrystalline materials. Within the industry, nanocrystalline materials are commonly defined as crystalline materials that have an average particle or grain size of less than 100 nanometers (0.1 micron). A deliberate distinction is made between nanocrystalline materials and submicron crystalline materials, which have an average particle or grain size of less than 1 micron.

The relative percentage of interfacial atoms to total atoms in a material increases dramatically with decreasing size below 100 nanometers (see Figure 1). The resultant properties of nanocrystalline materials thus have a much greater dependence on the contributions of interfacial atoms (those atoms on the surface of a particle or in the grain boundaries of a consolidated material) than submicron materials. Some unconventional mechanical, chemical, electrical, optical and magnetic properties exhibited by nanocrystalline materials are attributed to this greater dependence on the contributions of interfacial atoms.

PROCESSING METHODS

A wide range of techniques have been developed to fabricate nanocrystalline materials. The most commonly practiced of these are gas-phase condensation, sol-gel chemistry, spray pyrolysis and hydrothermal processing. The challenge with all techniques is to successfully scale

production to commercial volumes of nanocrystalline materials with properties and economies that allow their use in mainstream applications. One of the first techniques to be so scaled, physical vapor synthesis, is based on the principles of gas-phase condensation.

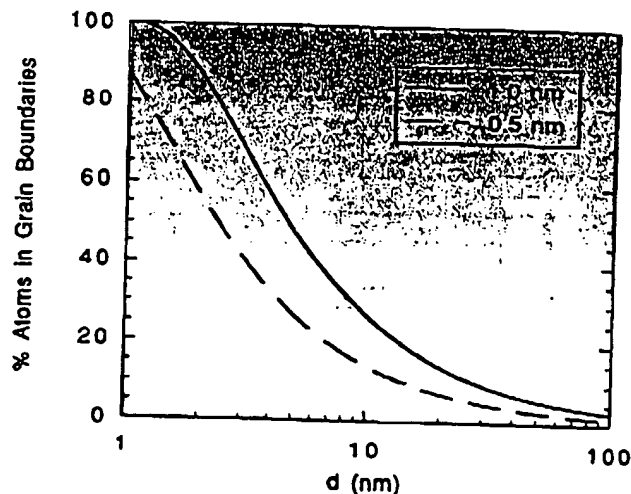
In the 1980s, gas-phase condensation was demonstrated to be capable of fabricating a wide range of ceramic and metallic nanocrystalline particles. Gas-phase condensation involves the evaporation of precursor materials in reduced-pressure, inert environments. After evacuating a chamber, inert gas is introduced to create the reduced-pressure environment. The

precursor material is then evaporated using any of a variety of energy sources.

Atoms of evaporated precursor collide with the cooler atoms of the inert backfill gas. These cooler gas atoms cause the evaporated precursor to condense and solidify as nanocrystalline particles of the precursor. If reactive gas is used for backfill instead of inert gas, the evaporated precursor and gas react, condense and solidify as nanocrystalline particles of the formed compound.

The cooling of the gas is caused by convective currents that are created within the chamber by the temperature gradient between the energy source and a

Figure 1



Percentage of atoms in grain boundaries of nanocrystalline material as a function of average grain size assuming grain boundary thickness range of 0.5 to 1 nanometer. (From R.W. Siegel, "Cluster-Assembled Nanophase Materials", *Annu. Rev. Mater. Sci.* 21, 559-578, 1991)

Figure 2

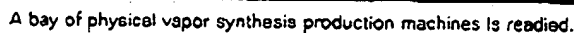


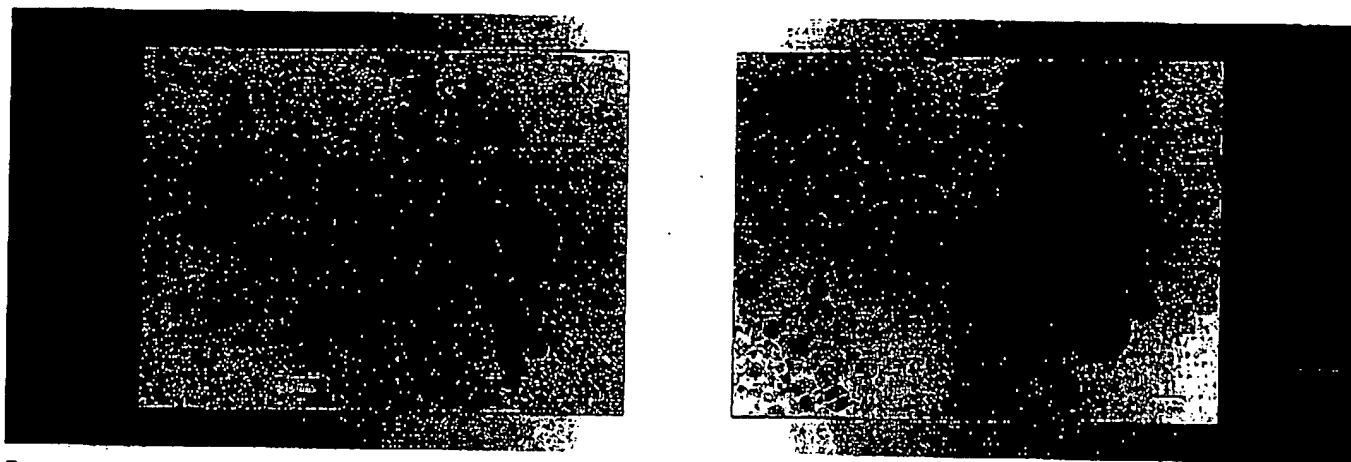
Figure 3



Cerium oxide produced by physical vapor synthesis is currently being evaluated as an additive to slurries for planarization of dielectric layers. Such slurries generally contain silica as the sole abrasive component. Initial tests indicate that adding a small percentage of cerium oxide to silica-based slurries can increase removal rates to four times the rates of slurries containing no cerium oxide. No concurrent degradation of defectivity, microscratching or uniformity have been detected.

A single physical vapor synthesis production machine is capable of delivering tens of kilograms of nanocrystalline materials per day. This provides economies that are feasible for a large

Figure 4



Transmission electron microscopy of yttrium oxide (left) and aluminum oxide (right) produced by physical vapor synthesis.

number of applications. The technique has already been successfully scaled to a production capacity exceeding 100 tons per year, and additional capacity can be added in a modular fashion as needed (see Figure 2).

COOLING REQUIRED

In physical vapor synthesis (Figure 3), precursor material is introduced at a controlled rate into a chamber. Within the chamber, a plasma arc is formed between a nonconsumable electrode and the consumable precursor. The precursor, typically a high-purity metal rod, passes through the plasma arc and is melted and vaporized.

A quench and/or reactive gas is introduced to the chamber. Atoms of evaporated precursor collide with the cooler atoms of the quench gas. The evaporated precursor condenses and solidifies as nanocrystalline particles of the precursor. If a reactive gas is also present, it reacts with the evaporated precursor, causing nanocrystalline particles of the resultant compound to be formed upon condensation and solidification.

After the nanocrystalline particles are solidified, their temperature is still elevated. The particles must be cooled to minimize agglomeration. Additional gas is turbulently introduced to accelerate cooling of the particles. The gas propels the particles into a collector housing. The collector housing contains filter media that allows the gas to exit but traps the weakly agglomerated nanocrystalline particles. The nanocrystalline particles

Advantages of Physical Vapor Synthesis

- ◆ Economical
- ◆ Narrow particle size distribution
- ◆ Continuous process
- ◆ Particle size control
- ◆ Nonporous, equiaxed particles
- ◆ High-purity materials
- ◆ Wide range of oxides

collect on the filter media in the collector housing and are periodically harvested.

PRODUCT CHARACTERISTICS

Numerous nanocrystalline oxides and noble metals have been successfully fabricated using physical vapor synthesis. These include aluminum oxide, titanium dioxide, zinc oxide, iron oxide, cerium oxide, yttrium oxide, copper oxide, magnesium oxide, manganese oxide, indium-tin oxide, palladium, silver, gold and platinum.

Non-noble metals are also of commercial interest in nanocrystalline form. However, in this size regime, the surfaces of these particles are highly reactive and will oxidize when exposed to air. In the case of some metals, this oxidation causes violent combustion. Several methods to stabilize particles are under development and are expected to allow eventual commercialization of these metals. Additionally, fabrication of such materi-

als as nanocrystalline carbides and nitrides will be attempted with modifications to the current physical vapor synthesis practices.

A metastable phase of a material generally results from physical vapor synthesis due to the high process temperatures and rapid solidification. Particle morphologies vary with material, although they are commonly equiaxed. Aluminum oxide particles produced appear perfectly spherical when imaged by SEM or TEM (see Figure 4).

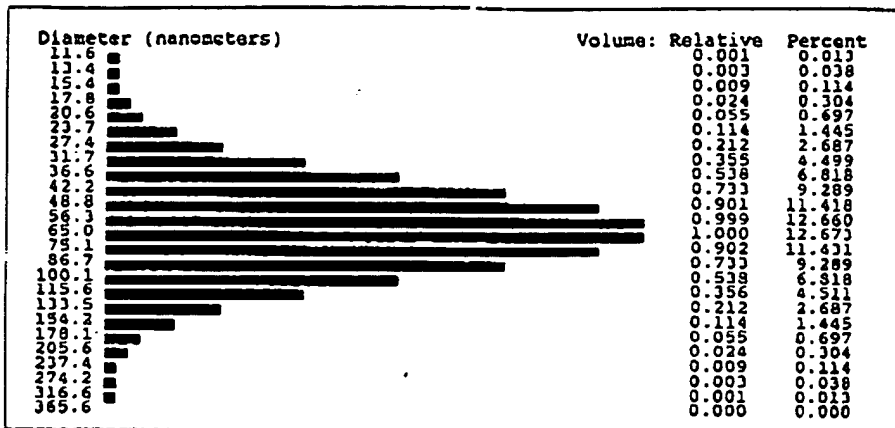
PARTICLE SIZE CONTROL

Physical vapor synthesis provides sufficient control to allow concurrent adjustment of the specific surface area and the average particle size of production materials. Specific surface areas can be varied from approximately 30 to 90 m²/g as desired. This corresponds to average particle sizes ranging from approximately 10 to 100 nanometers. Based on close correlation between average particle sizes measured from TEM images and calculated from BET specific surface areas, physical vapor synthesis particles are virtually nonporous.

More important than the average particle size in most applications is the particle size distribution, specifically the upper end of the distribution. Physical vapor synthesis materials have lognormal distributions, with one endpoint at a few nanometers and another between 300 and 500 nanometers (see Figure 5). Less than 1% of the particles are above 150 nanometers.

Nanocrystalline Materials

Figure 5



Volume-weighted particle size distribution of aluminum oxide produced by physical vapor synthesis.

When the particles are collected from physical vapor synthesis, they are weakly agglomerated up to tens of microns. The agglomerates can be broken down to the particle size distributions described above by such techniques as ultrasonication and

media milling. Further refinement of these particle size distributions is also possible, eliminating particles above a specific size.

The overall purity of physical vapor synthesis nanocrystalline particles

approximates the purity of the precursor material. Consequently, precursors commensurate with the overall purity requirements of the application are used. Specific impurities of concern for a given application can be engineered to desired levels.

APPLICATIONS

Applications for oxide particles produced by physical vapor synthesis have already been commercialized and include abrasives in polishing slurries for semiconductors, anti-fungal agents for health care and additives to increase the wear resistance of polymers. Additional applications for oxide and noble metal particles are also being developed. These include transparent conductive coatings, precious metal catalysts and additives to provide various functionalities to polymers. □

Periodic Table of Elements

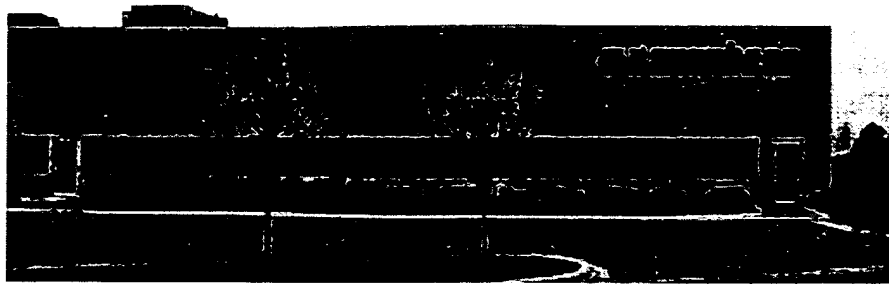
& Nanocrystalline Compounds Available from Nanophase Technologies

Periodic Table of Elements

& Nanocrystalline Compounds Available from Nanophase Technologies

Available in Nanocrystalline form from Nanophase.
Contact Nanophase regarding custom Nanocrystalline ordering.

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Nanophase Technologies Corporation is the world's leader in the development, production, and marketing of nanocrystalline materials for a wide range of industrial applications.

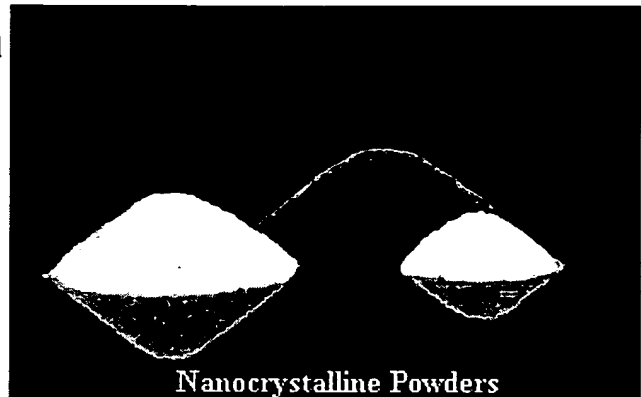
This web site is designed to provide information on our company, our technologies, our products, and applications for our nanocrystalline materials . We hope that you will visit this site often.

Corporate History

The origin of Nanophase can be traced back to research performed during the 1980s at Argonne National Laboratory, a U.S. Department of Energy facility. Interested in studying the properties of nanocrystalline materials, researchers at Argonne conceived a unique process to fabricate them. This process, commonly referred to today as gas phase condensation, could produce small quantities of materials with unique characteristics. Besides their sizes being measured in nanometers, the particles were of high purity, had no residual surface contaminants, were spherical, and were non-porous.

Convinced that these materials were commercially important and that gas phase condensation could be scaled to produce them in large quantities at reasonable cost, Argonne scientist Dr. Richard Siegel founded Nanophase in 1989. At that time, gas phase condensation could produce only a few grams of nanocrystalline material per day at a cost of approximately \$1,000 per gram.

Several years of effort by scientists at Nanophase resulted in the development of a new process based generally on the principles of gas phase condensation, but with significantly improved fabrication rates and economies. This process, named Physical Vapor Synthesis (PVS) now allows Nanophase to produce tons of materials per year with costs as low as a few pennies per gram. PVS is patented and was recognized with an R&D 100 Award in 1995 as one of the year's most technologically significant new developments.



Nanocrystalline Powders

NanoTek® Aluminum Oxide

Product Code: 0100

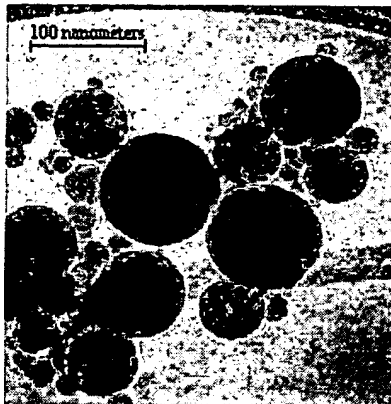
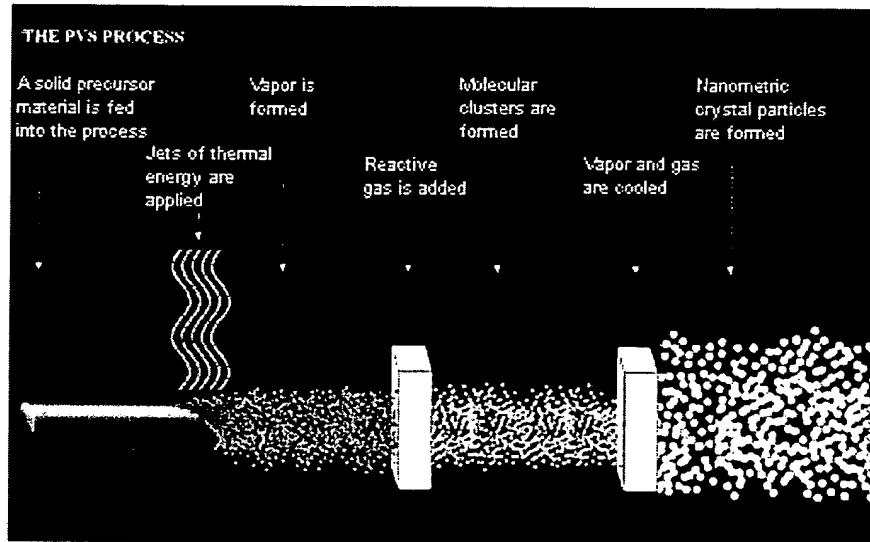
Molecular Formula	Al ₂ O ₃
Purity	99.5+%
Average Particle Size	27 - 56 nm (from SSA)
Specific Surface Area	30 - 60 m ² /g (BET)
Morphology	<u>Spherical</u>
Crystal Phase	Gamma
Distribution	<u>2 - ~400 nm</u> (by laser scattering, Horiba LA-910)
Refractive Index	1.7
Appearance	White to off white powder
Bulk Density	0.10 g/cc
True Density	3.6 g/cc

Pricing	
Unit Size	Price
25g	\$19.00
50g	\$27.00
100g	\$39.00
250g	\$64.00
500g	\$85.00
1kg	\$135.00
2kg	\$200.00
>2kg	<u>Quote</u>

Physical Vapor Synthesis (PVS)

Nanophase primarily employs its patented Physical Vapor Synthesis (PVS) process to produce nanocrystalline particles. PVS utilizes a plasma to heat a selected metal precursor in open atmosphere. As the temperature rises, the metal's atoms boil off into a stream of flowing gas, creating a vapor.

Collisions with atoms of a gas that is introduced to the process cool the metal atoms so that the vapor condenses into liquid molecular clusters. Cooling continues, freezing these molecular clusters into solid particles of nanometric size. The flowing gas transports the particles to a collection vessel. The presence of oxygen allows oxygen atoms to intermingle with metal atoms forming nanocrystalline metal oxides such as aluminum oxide and titanium dioxide.

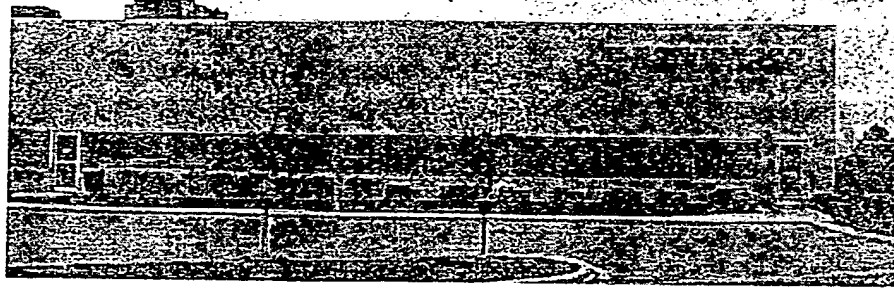


TEM of NanoTek Aluminum Oxide
produced using PVS

The resultant powder consists of weakly agglomerated particles of spherical morphology. Purity of the powders is primarily dependent upon the purity of the precursor material. There are no residual chlorides or sulfides present on the surfaces of the particles as there are with materials produced by certain other combustion techniques. The clean nature of these surfaces enable treatments to be applied to tailor these materials for applications requiring dispersion in a variety of fluids.

Nanophase developed PVS from the general principles of a process known as gas phase condensation. Gas phase condensation is conducted under high vacuum conditions which limit it to producing research scale quantities of nanocrystalline materials. It typically employs a resistive heat source to generate a gas phase of the precursor material. Cooling of this gas phase to cause condensation and freezing to form nanocrystalline particles is accomplished using a liquid-nitrogen cooled collection surface. The materials produced by gas phase condensation are similar in morphology, purity, and size to those produced via PVS.

Gas phase condensation is practiced by many research scientists around the world as a means of fabricating materials for their experiments. Nanophase's patented PVS process is the only known method by which commercial quantities of these materials can be produced.



Nanophase Technologies Corporation is the world's leader in the development, production, and marketing of nanocrystalline materials for a wide range of industrial applications.

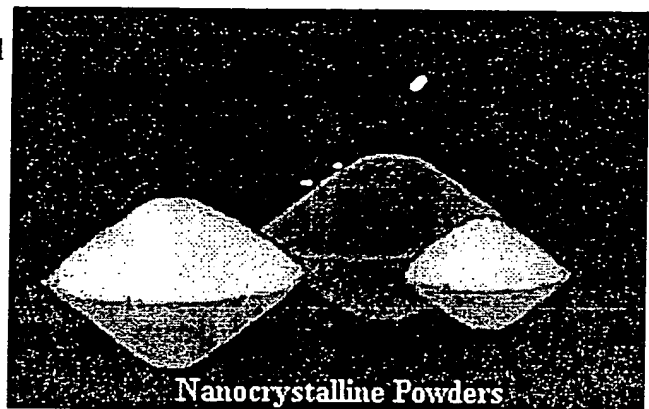
This web site is designed to provide information on our company, our technologies, our products, and applications for our nanocrystalline materials . We hope that you will visit this site often.

Corporate History

The origin of Nanophase can be traced back to research performed during the 1980s at Argonne National Laboratory, a U.S. Department of Energy facility. Interested in studying the properties of nanocrystalline materials, researchers at Argonne conceived a unique process to fabricate them. This process, commonly referred to today as gas phase condensation, could produce small quantities of materials with unique characteristics. Besides their sizes being measured in nanometers, the particles were of high purity, had no residual surface contaminants, were spherical, and were non-porous.

Convinced that these materials were commercially important and that gas phase condensation could be scaled to produce them in large quantities at reasonable cost, Argonne scientist Dr. Richard Siegel founded Nanophase in 1989. At that time, gas phase condensation could produce only a few grams of nanocrystalline material per day at a cost of approximately \$1,000 per gram.

Several years of effort by scientists at Nanophase resulted in the development of a new process based generally on the principles of gas phase condensation, but with significantly improved fabrication rates and economies. This process, named Physical Vapor Synthesis (PVS) now allows Nanophase to produce tons of materials per year with costs as low as a few pennies per gram. PVS is patented and was recognized with an R&D 100 Award in 1995 as one of the year's most technologically significant new developments.



NanoTek® Aluminum Oxide

Product Code: 0100

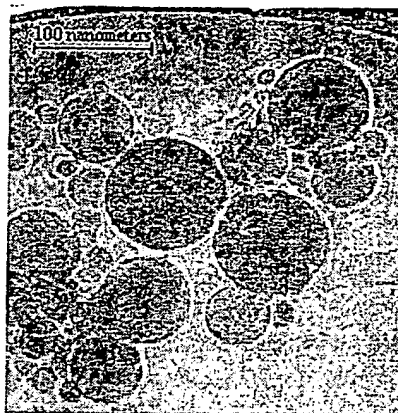
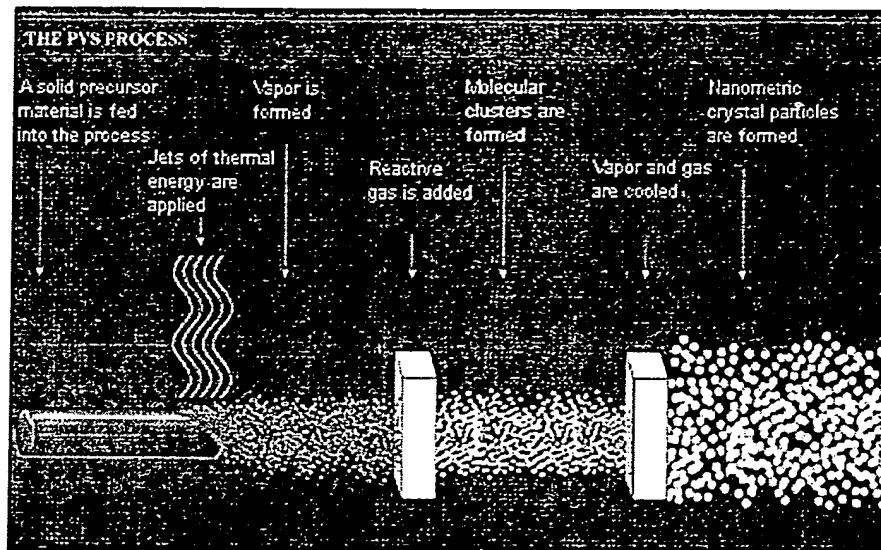
Molecular Formula	Al ₂ O ₃
Purity	99.5+%
Average Particle Size	27 - 56 nm (from SSA)
Specific Surface Area	30 - 60 m ² /g (BET)
Morphology	<u>Spherical</u>
Crystal Phase	Gamma
Distribution	<u>2 - ~400 nm</u> (by laser scattering, Horiba LA-910)
Refractive Index	1.7
Appearance	White to off white powder
Bulk Density	0.10 g/cc
True Density	3.6 g/cc

Pricing	
Unit Size	Price
25g	\$19.00
50g	\$27.00
100g	\$39.00
250g	\$64.00
500g	\$85.00
1kg	\$135.00
2kg	\$200.00
>2kg	<u>Quote</u>

Physical Vapor Synthesis (PVS)

Nanophase primarily employs its patented Physical Vapor Synthesis (PVS) process to produce nanocrystalline particles. PVS utilizes a plasma to heat a selected metal precursor in open atmosphere. As the temperature rises, the metal's atoms boil off into a stream of flowing gas, creating a vapor.

Collisions with atoms of a gas that is introduced to the process cool the metal atoms so that the vapor condenses into liquid molecular clusters. Cooling continues, freezing these molecular clusters into solid particles of nanometric size. The flowing gas transports the particles to a collection vessel. The presence of oxygen allows oxygen atoms to intermingle with metal atoms forming nanocrystalline metal oxides such as aluminum oxide and titanium dioxide.



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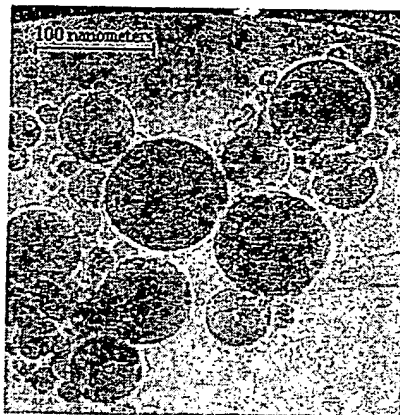
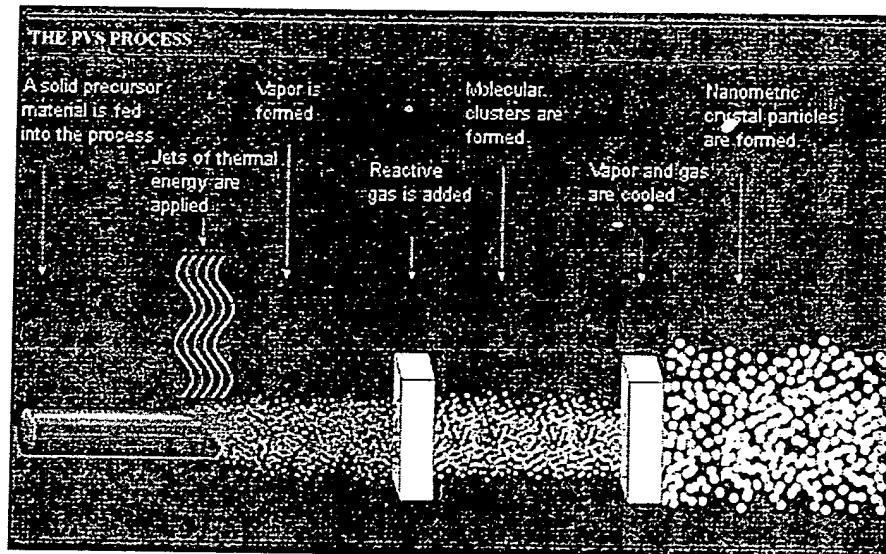
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APPENDIX E

1. Declaration and Resume of Dr. Nobuyuki Kambe,
coinventor of present application, from parent application
09/136,483.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Kumar et al.

Applic No.: 09/136,483

Filed : August 19, 1998

For : ALUMINUM OXIDE PARTICLES

Docket No.: N19.12-0016

Group Art Unit:
1755Examiner: M. -
Marcheschi

DECLARATION UNDER 37 C.F.R. §1.132

BOX AF
Assistant Commissioner for Patents
Washington, D.C. 20231I HEREBY CERTIFY THAT THIS PAPER IS
BEING SENT BY U.S. MAIL, FIRST
CLASS, TO THE ASSISTANT
COMMISSIONER FOR PATENTS,
WASHINGTON, D.C. 20231, THIS01 DAY OF May, 2000.
Robert S. Gaud
PATENT ATTORNEY

I, Nobuyuki Kambe, hereby declare as follows:

1. I am presently Vice President, Market Development at NanoGram Corporation.
2. I am a founder of NanoGram Corporation, and I have been a Vice President at NanoGram since it was founded in 1996. I have a Bachelor of Science degree and a Master of Science degree in Instrumentation Engineering from Keio University and a Ph.D. in Electrical Engineering from Massachusetts Institute of Technology in 1982.
3. Prior to my employment at NanoGram, I was Senior Managing Director with the International Center for Materials Research (ICMR), a consortium of prominent Japanese companies working jointly on the development of advanced materials. My duties at ICMR included instituting a research and development program in functional polymers and a research and a program in nanoparticles, which was the predecessor of NanoGram. Prior to working with ICMR, I held several positions with Nippon Telephone and Telegraph including Senior Research Scientist and Senior Manager.

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4. I have considerable experience in advanced materials research and in particular on nanoparticles and nanomaterials. During my employment with NanoGram, I have worked closely with materials development at NanoGram, and I have also worked extensively with outside companies, consultants and academic researchers toward the development of particular markets and new areas for research related to nanoparticles.

5. I am very familiar with various approaches for producing nanoscale particles, characterization of these particles and the public availability of nanoscale particles with various properties. A successful founder of a technology driven company working in the area of nanoparticles is required to have such knowledge.

6. I am an inventor on the above referenced patent application.

7. I have read all of the references cited by the patent Examiner in the Office Action mailed on February 29, 2000. None of the particle synthesis approaches described in these references is capable of producing nanoparticles having the narrow particle size distribution of the claims pending in the present patent application. Furthermore, I am aware of no approaches that are available to separate nanoscale particles having an average particle size less than about 500 nm to produce a collection of particles with the claimed narrow particle size distribution. In addition, since the approaches described in the cited patents are not capable of producing nanoparticles with narrow particle size distributions, a person of ordinary skill in the art would not have thought, as of our filing date, that the claimed collections of particle would be obvious over the disclosure provided in these references.

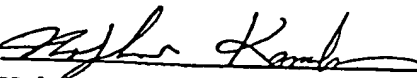
8. I am aware of no methods other than the process described in our above noted patent application for producing aluminum oxide nanoparticles having an average particle size less than about 500 nm with the narrow particle size distributions specified in our

-3-

pending claims.

9. I declare that all statements made herein that are of my own knowledge are true and that all statements that are made on information and belief are believed to be true: and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: May 1, 2000

By: 
Nobuyuki Kambe, Ph.D.

NOBUYUKI KAMBE

840 Hobart Avenue
Menlo Park, CA 94025 USA
Tel. 1-650-322-6832
E-mail kambe@nanogram.com

EDUCATION

1976 - 1982 Massachusetts Institute of Technology Cambridge, MA

Doctor of Philosophy in Electrical Engineering

- Dissertation in graphite intercalation materials and their structural behavior
- Visiting researcher at National Magnet Laboratory

1974 - 1976 Keio University

Tokyo, Japan

Master of Science, Instrumentation Engineering

- Observation of novel phase transition in ultra-thin Au film over C film

1970 - 1974 Keio University

Tokyo, Japan

Bachelor of Science, Instrumentation Engineering

- Percolation model over the surface of insulators

PROFESSIONAL EXPERIENCE

1996 - Present NanoGram Corporation

Fremont, CA

Vice President, Market Development

- Identification, development and planning of new business opportunities for NanoGram particles

1994 - 1996 International Center for Materials Research Kawasaki, Japan

Senior Managing Director

- Creation of functional polymer R&D
- Creation of nanoparticle R&D at Lexington, KY as precursor of NanoGram

1981 - 1994 Nippon Telegraph & Telephone (NTT)

Tokyo, Japan

1991 - 1994 *Senior Manager at Corporate HQ*

- Strategic corporate planning of new businesses for all NTT technologies
- Completion of technology management course at Japan Productivity Ctr

1989 - 1991 *Senior Research Scientist and Supervisor at Basic Res. Lab.*

- Nonlinear optical materials: synthesis, MBE (molecular beam epitaxy) machine build-up, nonlinear optics measurements
- NTT Basic Res. Lab. Director Award

1984 - 1989 Staff Research Scientist

- Semiconductor superlattice laser devices: GaAs & GaSb-type, device fabrication process development
- Layered semiconductors: GaSe & InSe-type, synthesis, MBE, electron diffraction and spectroscopy, TEM
- Total renovation of high-power x-ray lab: planning and completion of 4 rotor-flex machine facility

1982 - 1989 Research Scientist

- Photosensitive materials: synthesis, optical characterization, nonlinear optical measurements

PATENTS AND PUBLICATIONS

Research interests include electronic and optical properties of low dimensional materials, graphite intercalation compounds, MBE-grown semiconductor thin films and new functional polymers and nanoparticle ceramics.

Ten (10) patents in nanomaterials.

Author of twenty publications and three books.

LANGUAGES

Japanese (mother tongue)

English (fluent)

REFERENCES

- Prof. Millie Dresselhaus, Institute Professor at MIT [617-253-6864]
 - Mr. William Hecht, CEO at MIT Alumni Association [617-253-8204]
 - Dr. Noriyoshi Osumi, VP at NTT America [650-903-0660]
 - Dr. Rikuo Takano, Executive Director at Mitsubishi Materials [011-81-422-72-2435]
 - Dr. Tatsuo Izawa, Executive Director at NTT [011-81-462-40-5000]
 - Dr. Tomoaki Yamada, Fellow at NTT Basic Res. Lab. [011-81-462-40-3350]
-

APPENDIX F

1. Claims from copending Application 08/961,735.
2. Claims from copending Application 09/266,202.

Claims of Copending Application 08/961,735

1. A polishing composition comprising a dispersion of particles, the particles comprising metal compounds and having an average particle diameter from about 5 nm to about 50 nm and a distribution of diameters such that at least about 95 percent of the particles have a diameter greater than about 60 percent of the average diameter and less than about 140 percent of the average diameter.

2. The polishing composition of claim 1 wherein the particles are dispersed in an aqueous solution.

3. The polishing composition of claim 1 wherein the particles are dispersed in a nonaqueous solution.

4. The polishing composition of claim 1 wherein the particles comprise a composition selected from the group consisting of SiO_2 , SiC , TiO_2 , Fe_3C , Fe_7C_3 , Fe_2O_3 , Fe_3O_4 , MoS_2 , MoO_2 , WC , WO_3 and WS_2 .

6. A method of smoothing a surface comprising the step of polishing the surface with the polishing composition of claim 1.

7. The method of claim 6 wherein the polishing is performed with a polishing pad.

8. The method of claim 6 wherein the polishing is performed with a motorized polisher.

9. A polishing composition comprising a dispersion of particles, the particles comprising metal compounds with an average particle diameter from about 5 nm to about 200 nm and a single crystalline phase with a uniformity of at least about 90 percent by weight.

9. The polishing composition of claim 1 having a single crystalline phase with a uniformity of at least about 90 percent by weight.

10. The polishing composition of claim 9 wherein the particles comprise a composition selected from the group consisting of SiO_2 , SiC , TiO_2 , Fe_3C , Fe_7C_3 , Fe_2O_3 , Fe_3O_4 , MoS_2 , MoO_2 , WC , WO_3 and WS_2 .

12. The polishing composition of claim 9 wherein the particles have a single crystalline phase with a uniformity of at least about 95 percent by weight.

13. The polishing composition of claim 9 wherein the particles have a single crystalline phase with a purity of at least about 99 percent by weight.

14. The polishing composition of claim 9 wherein the particles have a single crystalline phase with a purity of at least about 99.9 percent by weight.

15. A polishing composition comprising a dispersion of particles, the particles comprising metal compounds or silicon compounds with an average particle diameter from about 5 nm to about 50 nm and effectively no particles with a diameter greater than about 5 times the average diameter.

16. A polishing composition comprising an aqueous dispersion of particles, the particles comprising metal carbides or metal sulfides and having an average particle diameter from about 5 nm to about 200 nm.

23. The polishing composition of claim 15 wherein the particles are dispersed in an aqueous solution.

25. The polishing composition of claim 16 wherein the particles have an average diameter from about 5 nm to about 100 nm.

26. The polishing composition of claim 16 wherein the dispersion includes from about 0.05 to about 5 percent by weight particles.

27. The polishing composition of claim 16 wherein the particles have an average diameter from about 5 nm to about 50 nm.

28. The polishing composition of claim 16 wherein effectively no particles have an diameter greater than about 5 times the average diameter.

29. The polishing composition of claim 16 wherein the metal carbides or metal sulfides comprise metal carbides.

30. The polishing composition of claim 29 wherein the metal carbides comprise Fe_3C , Fe_7C_3 , or WC.

31. The polishing composition of claim 29 wherein the metal carbides comprise SiC.

32. The polishing composition of claim 16 wherein the metal carbides or metal sulfides comprise metal sulfides.

33. The polishing composition of claim 16 wherein the particles have a distribution of diameters such that at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

34. The polishing composition of claim 16 wherein the particles have a distribution of diameters such that at least about 95 percent of the particles have a diameter greater than about 60 percent of the average diameter and less than about 140 percent of the average diameter.

CLAIMS FROM COPENDING APPLICATION 09/266,202

1. A collection of particles in a powder comprising crystalline zinc oxide, the collection of particles having an average diameter less than about 95 nm and a distribution of particle sizes such that at least 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.
2. The collection of particles of claim 1 wherein the collection of particles have an average diameter from about 5 nm to about 50 nm.
3. The collection of particles of claim 1 wherein the collection of particles have an average diameter from about 5 nm to about 25 nm.
4. The collection of particles of claim 1 wherein effectively no particles have a diameter greater than about four times the average diameter of the collection of particles.
5. The collection of particles of claim 1 wherein effectively no particles have a diameter greater than about three times the average diameter of the collection of particles.
7. An electrical resistor component comprising the collection of particle of claim 1.
8. The electrical resistor component of claim 7 wherein the component is a varister.
9. The electrical resistor component of claim 8 wherein the varister has a non-linear voltage dependance.
25. The collection of particles of claim 1 wherein effectively no particles have a diameter greater than about two times the average diameter of the collection of particles.
26. The collection of particles of claim 1 wherein at least 95 percent of the particles have ratios of the dimension along the major axis to the dimension along the minor axis less than about 2.
27. The collection of particles of claim 1 wherein the zinc oxide has a stoichiometry of ZnO.
28. The collection of particles of claim 1 wherein the zinc oxide has a stoichiometry of ZnO₂.

29. The collection of particles of claim 1 wherein the zinc oxide has a Zincite crystal structure.
30. The electrical resistor component of claim 7 further comprising metal/silicon oxide particles selected from the group consisting of Bi_2O_3 , Sb_2O_3 , SiO_2 , Co_2O_3 , and MnO_2 .
31. A display device comprising the collection of particles of claim 1.
32. The display device of claim 31 wherein the display device comprises a cathode ray tube.
33. The display device of claim 31 wherein the display device comprises a flat panel display.
34. The display device of claim 33 wherein the flat panel display comprises a field emission device.
35. The display device of claim 33 wherein the flat panel display comprises an electroluminescent display.